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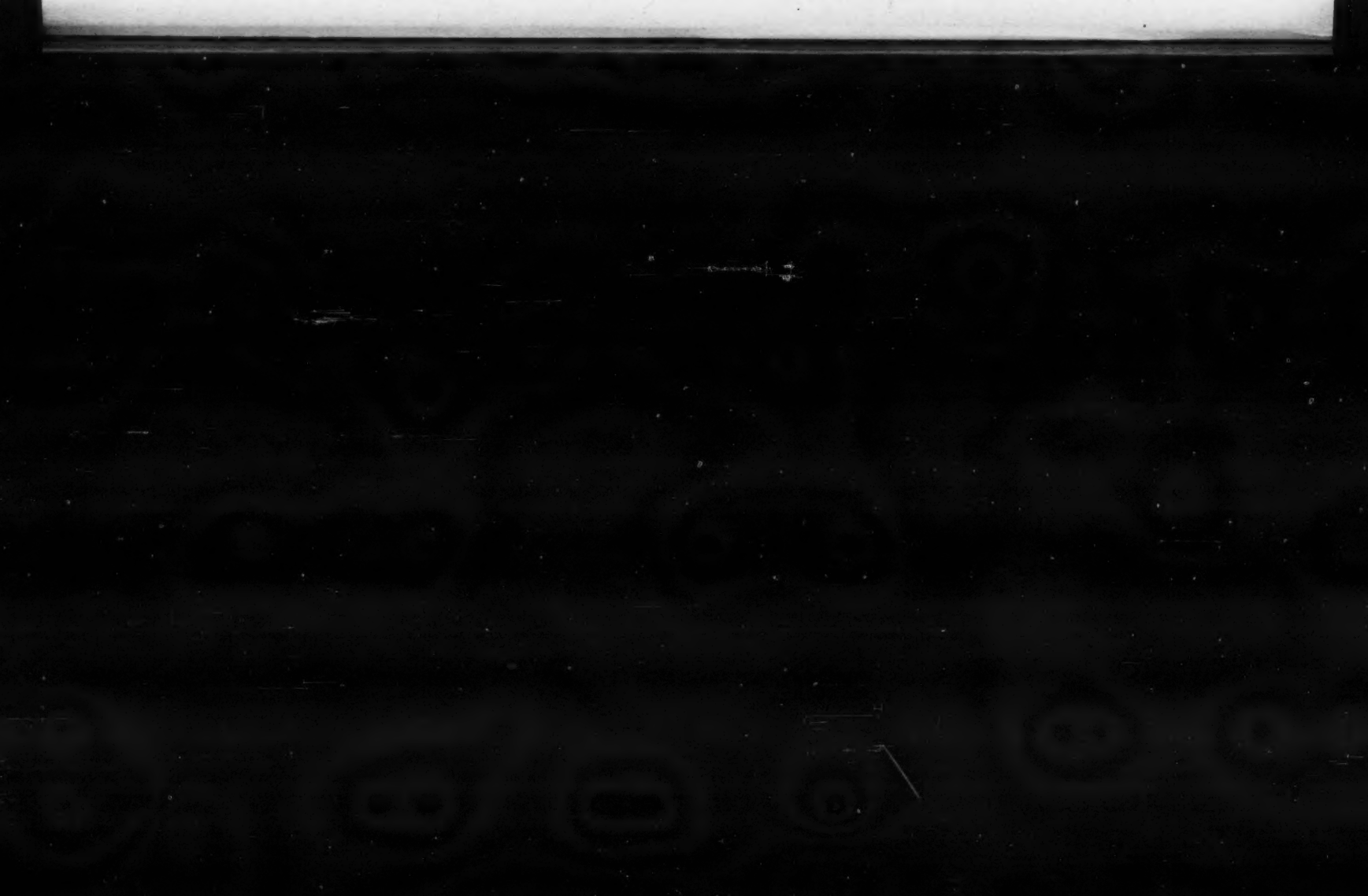

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VOL. 29 APRIL, 1951 NUMBER 4

DRIED WHOLE EGG POWDER

XXIX. THE EFFECT OF HIGH MOISTURE CONTENT ON FLUORESCENCE AND OTHER CHEMICAL CHANGES[1]

BY M. BOULET[2] AND JESSE A. PEARCE[3]

Abstract

Calculations based on the rate of fluorescence development in glucose–glycine mixtures indicated that fluorescence development in stored egg powders containing about 8% moisture should be more rapid than in stored powders of higher or lower moisture content. Fluorescence measurements on egg powders adjusted to various moisture levels from 3% to 16% verified this calculation. Rate of decrease of reducing sugar content behaved similarly. Measurements of the decrease in solubility of nitrogenous components indicated that this change was not directly related to the reactions that produce fluorescing substances.

Introduction

In studies on stored biscuits, fluorescence development was greater at about 12% moisture than at higher or lower moisture levels (5). Previously published work showed that the rate of fluorescence development in egg powder increased with increases in moisture content up to about 8% (11), but no data existed for higher moisture contents. Measurements of fluorescence changes in mixtures of glucose and glycine indicated that there was an optimum moisture content at which fluorescence developed most rapidly (8); therefore, since the reactions producing fluorescent materials in egg powder and in mixtures of glucose and glycine appear to be similar in nature (2, 7, 8), it should be possible to calculate the moisture content at which the most rapid development of fluorescing substances occurs in egg powder. This paper presents: calculations which show that fluorescing substances should develop more rapidly in egg powder containing 8% moisture than in powder at higher or lower moisture levels; fluorescence measurements which verify these calculations; and comparisons of fluorescence changes with changes in reducing sugar and in soluble nitrogenous components.

[1] *Manuscript received in original form, May 15, 1950, and, as revised, December 20, 1950. Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as paper No. 258 of the Canadian Committee on Food Preservation and as N.R.C. No. 2353.*

[2] *Biochemist, Food Investigations.*

[3] *Formerly Biochemist, Food Investigations; present address: Health Radiation Branch, Atomic Energy Division, National Research Laboratories, Chalk River, Ont.*

Calculation of Critical Moisture Content for Development of Fluorescing Substances in Egg Powder

With the aid of data available from model systems it is possible to compute the approximate moisture content at which fluorescing substances will develop in egg powder at a maximal rate.

It has been shown experimentally (8) that fluorescing substances developed most rapidly in glucose–glycine mixtures that contain 1.5 parts of water to 1.0 part of glucose and an excess (0.5 part) of glycine, and it has been suggested that water is required only for the first step in this reaction, i.e., the hydration of the aldehyde (3). Egg powder contains 1.35% of reducing materials (as glucose) in a form that enters into reactions with amines. If reactions in glucose–glycine mixtures and egg powder are similar, then the optimum amount of water for the development of fluorescing substances from the reducing material in 100 gm. of egg powder will be about 2 gm. (i.e., 1.35×1.5).

The reaction occurs at active centers in egg powder (8), and fat, excess protein, and water (beyond a certain critical figure) can be assumed to act as diluents with respect to these active centers. As egg powder is made up of a number of small particles, dilution of the active centers can be considered to be extended linearly. The distance between active centers in egg powder, as compared with glucose–glycine mixtures, is increased by a factor of $\left(\frac{100 - 1.35}{1.35}\right)^{1/3} \cong 4$. Thus, the amount of water required to attain the maximum rate of fluorescence development in egg powder is $2 \times 4 = 8\%$.

Materials and Methods

A sample of egg powder produced in a box-type drier (powder B) and one produced in a cone-type drier (powder C) were adjusted to moisture contents from 3.3% to 16.5%. This range of moisture levels was obtained by dispersion of the powders in petrol ether (b.p. 68° to 104°F.) in a Waring blendor, addition of the desired weight of water (allowance was made for subsequent moisture loss by evaporation), and evaporation of the petrol ether at room temperature. During evaporation, the material was agitated in a Mixmaster to disperse the fat through the powder particles.

The prepared powders were stored in tightly closed screw-cap jars at 80°, 100°, 120°, and 140°F. Some untreated powders and some powders dispersed in petrol ether only were included to evaluate effects attributable to dispersion in ether. Initial samples, samples held for 6 and 21 days at 80° and 100°F., and samples held for one, two, and three days at 120° and 140°F. were examined for fluorescing materials, reducing sugar content, and solubility of nitrogen-containing components.

Fluorescing materials were extracted with a 10% potassium chloride solution from chloroform-defatted egg powder, and determined as units on the scale of a Coleman fluorometer with the B-1 and PC-1 filters (9).

Reducing sugar was determined in a dialyzate by Somogyi's volumetric method (1). To obtain the dialyzate, 20 ml. of a suspension of 10 gm. of powder shaken for one hour in 92 ml. of 10% potassium chloride solution was pipetted into a bag made from Visking dialyzing tubing. The bag was agitated for 16 hr. in a glass cylinder (3.5 cm. in diameter and 30 cm. long) containing 80 ml. of 10% potassium chloride solution.

Another aliquot of the suspension was diluted 1:5 with 10% potassium chloride solution and centrifuged to give a supernatant liquid in which soluble nitrogen was determined by a micro-Kjeldahl method (6).

Results

Results for the two types of powder differed only in minor aspects, and any effect attributable to dispersion in petrol ether was undeterminable.

Fig. 1 shows that, for all temperatures studied, the rate of development of fluorescing substance (recorded as the time required to attain a fluorescence value of 50 units) increased with increases in moisture content up to about 8% as shown elsewhere (11), and was maximal at about 8% moisture as predicted. Decrease in rate of fluorescence development with increase in moisture above

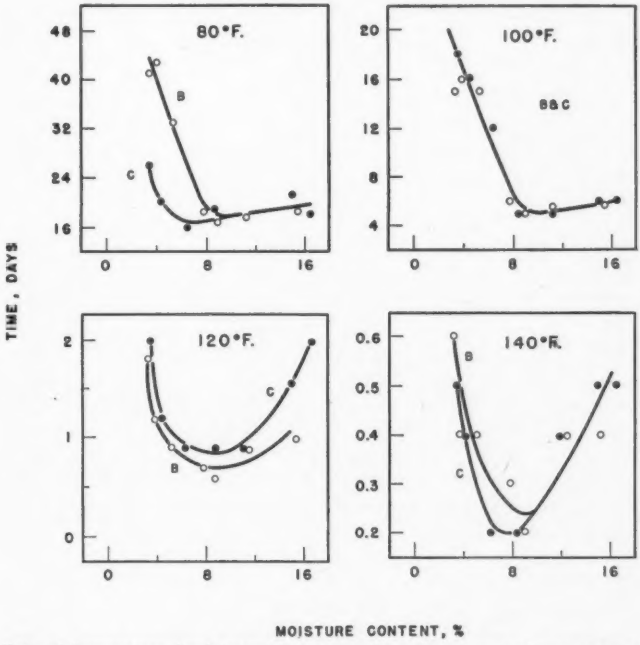

FIG. 1. *Rate of fluorescence development in egg powders of various moisture contents. Rate is recorded as the time required to attain a fluorescence value of 50 units. Powder B was produced in a box-type dryer and powder C in a cone-type dryer.*

8% was less marked at 80° and 100°F. than at 120° and 140°F. This was attributed to differences in plateaux in the relation between water-vapor pressure and moisture content of egg powder at the different temperature levels (cf. 4).

Fig. 2 shows that changes in the rate of loss of reducing sugar (recorded as the time required for the sugar to decrease to half its original value) were similar to changes in the rate of fluorescence development at all temperatures.

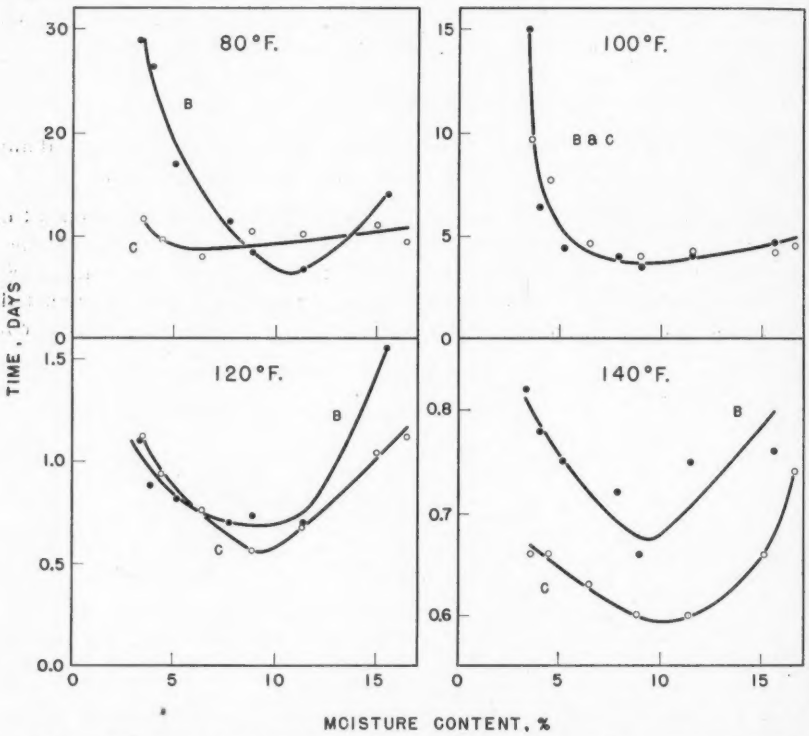

FIG. 2. *Rate of loss of reducing sugar in egg powders of various moisture contents. Rate is recorded as the time required for the sugar to decrease to half of its original value. Powder B was produced in a box-type dryer and powder C in a cone-type dryer.*

Losses in reducing sugar content and increases in fluorescing substances had already been associated by indirect evidence (2, 7, 8). These results show direct evidence of their association.

There is no direct evidence of the specific amino acid (or acids) involved in the reaction producing fluorescence changes in egg powder. In the present work, measurements of amino nitrogen indicated that amounts lost during storage were not detectable because of variability in sampling and measurement. How-

ever, total solubility, which is directly related to solubility of nitrogen-containing materials, is inversely related to fluorescence value (10). Therefore, the time required to reduce the nitrogen-containing solubles by 5% was used to examine the role of nitrogenous components in fluorescence development. With the exception that powder from the box-type drier did not decrease in nitrogen soluble components during storage for 21 days at 80°F., Fig. 3 shows that at

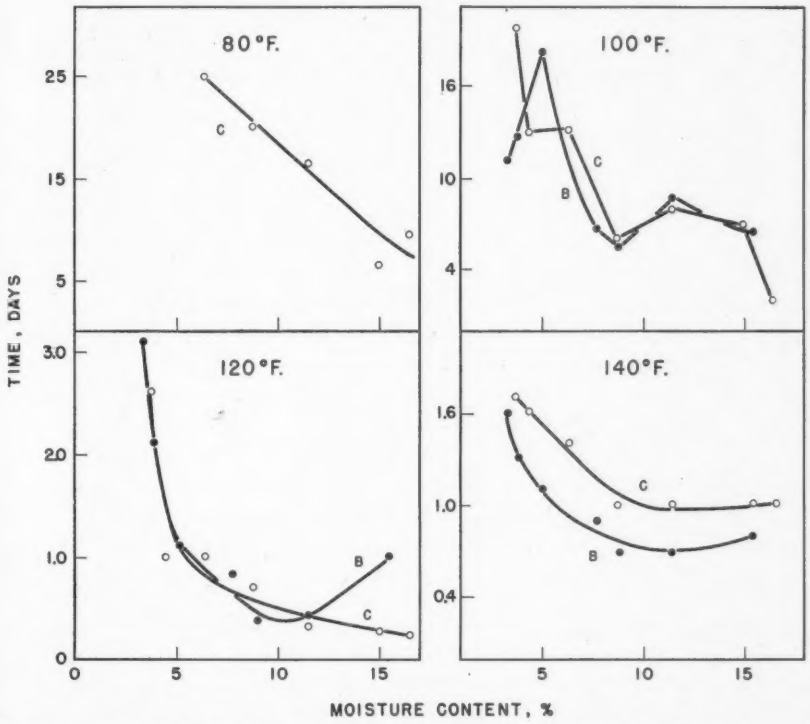

FIG. 3. *Rate of solubility change in egg powder of various moisture contents. Rate is expressed as the time required to reduce solubility of the nitrogen-containing materials by 5%. Powder B was produced in a box-type dryer and powder C in a cone-type dryer.*

80° and 100°F. the rate of decrease in solubility increased with increasing moisture from 3% to 16%, and that at 120° and 140°F. the rate increased with increasing moisture from 3% to 10% but remained relatively constant for moisture contents from 10% to 16%. These results indicate that decrease in solubility of nitrogenous materials in egg powder is not directly related to the reactions by which fluorescing materials are produced, and that solubility of these components of stored egg powder requires further study. This work is in progress in these laboratories.

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A FIELD METHOD FOR THE DETERMINATION OF HALOGENATED HYDROCARBONS[1]

By P. E. Braid and Kingsley Kay

Abstract

A small portable field instrument has been developed for the estimation of methyl bromide in air. By means of a squeeze bulb a measured amount of test air is forced through a reaction tube containing a mixture of iodine pentoxide and fuming sulphuric acid, the free bromine so liberated being brought into contact with a fluorescein-treated test paper to produce a color reaction. The test paper holder is of special design to produce uniform color. The instrument has been calibrated and provided with a color card to indicate concentrations of methyl bromide from 0 to 150 parts per million by volume in air. Trichloroethylene, carbon tetrachloride and higher concentrations of methyl bromide are determined by modifying the instrument and method.

Introduction

Methyl bromide in concentrations above 20 parts per million (p.p.m.) by volume in air may constitute a health hazard if inhaled daily over an eight-hour working period. It is therefore important in industrial health control to have a simple means of estimating small amounts of this material under conditions of field use such as in fumigation.

Existing analytical methods for methyl bromide involve its decomposition either by hydrolysis, with ethanolamine, sodium alcoholate, or alcoholic potash (3, 4, 10, 17), or pyrolysis (12, 15, 18, 19), and estimation of the product formed (HBr, NaBr, or Br_2) either argentometrically (4, 10, 12, 17), electrometrically (15, 19), or iodometrically (3, 15, 17, 18). Such methods are not adapted to field use. Two possible field methods have been reported; one by Lubatti (11) involves pyrolysis in a small tube and detection of the bromine formed by color reaction on a perforated disc treated with fluorescein. Its disadvantages are the fire hazard due to the combustion tube and nonuniform color production on the discs which handicap quantitation. The other field instrument is the halide lamp (17) which is widely used for detection of leaks in halogenated hydrocarbon refrigeration systems. Though this instrument is simple to operate its open flame creates a fire hazard and drafts make for wide variation in response. The present instrument eliminates fire hazard and permits calibration with good reproducibility. The method has been found adaptable for determination of trichloroethylene, carbon tetrachloride, and higher concentrations (500-10,000 p.p.m.) of methyl bromide.

Determination of Methyl Bromide

To eliminate fire hazard and permit quantitative estimation of methyl bromide under field conditions a chemical decomposition with associated color

[1] *Manuscript received October 17, 1950.*
Contribution from Industrial Health Laboratory, Department of National Health and Welfare, Ottawa, Canada.

test was considered the most promising avenue of investigation. Furthermore, various color tests for bromine were available. Accordingly the conversion of methyl bromide to bromine was explored.

Chemical hydrolysis as a means of methyl bromide decomposition is slow and yields bromide which is less conveniently determined by a color reaction than bromine. Oxidation by conventional agents could not be satisfactorily effected but it was found that iodine pentoxide – fuming sulphuric acid mixture originally developed for carbon monoxide detection (8, 9) would convert methyl bromide to bromine in high yields when packed on pumice in glass tubes. Aqueous fluorescein (1) was chosen as the color-producing reagent since it was found stable to the sulphur trioxide fumes evolved by the oxidizing mixture.

Owing to the presence of sulphur trioxide, direct reaction of fluorescein and bromine to produce color was not possible. Addition of sodium hydroxide was necessary for color development and a series of experiments established best reaction conditions. Mixed fluorescein and sodium hydroxide would not yield intensity of color obtained by use of separate solutions; 0.006% fluorescein* and 20% (by weight) sodium hydroxide gave best response.

Various media were studied for engaging fluorescein in reaction with bromine contained in air drawn through the oxidizing tube. Paper discs were finally selected. Supported in a special holder described below, these were soaked with 0.015 ml. of the fluorescein solution from a calibrated dropper, exposed to the bromine-laden air, and treated with one drop (0.028 ml.) of sodium hydroxide solution. Colors from greenish yellow (zero methyl bromide) to strong pink (150 p.p.m. methyl bromide in air) were highly uniform and reproducible if compared with standards within 45 sec.

Apparatus and Method

The apparatus developed for performing the determination in the field is shown diagrammatically in Fig. 1. A rubber squeeze bulb B, of volume 67 ml., is equipped with valves A and D by means of which test air is aspirated and forced through the tube E containing the reaction mixture. The reaction tube is fitted between the two rubber gaskets F by sliding the adjustable frame C, G, H. The air and volatile oxidation products are carried into the test disc holder J, K.

The test disc holder is shown in more detail in Fig. 2. The holder (3) screws into the frame (1) and is recessed to admit the rubber gasket (2) ($\frac{1}{2}$ in. of $\frac{1}{4}$ in. O.D. rubber tubing with smooth walls). The test disc (5) is held in place by the annular screw cap (6). A series of eight evenly spaced holes 0.018 in. in diameter and located 0.020 in. from the plane of the test disc are the special feature of the disc holder. The bromine-laden air moves through the conical passage and impinges against the disc. Part of the air passes through the disc and part passes out through the holes after contacting the under side of the

** The fluorescein solution was prepared by dissolving 0.1 gm. fluorescein in 5 ml. 10% sodium hydroxide and diluting to 100 ml. with water; 6 ml. of this solution was diluted to 100 ml. with water.*

disc. With this arrangement uniformly colored discs are obtained. The location, diameter, and number of holes determine the sensitivity and uniformity of the test.

The chemical oxidizing agent is prepared by mixing 3.5 gm. dehydrated iodine pentoxide with 9.5 gm. pumice (Pass 20 stop 35 grain size) and adding

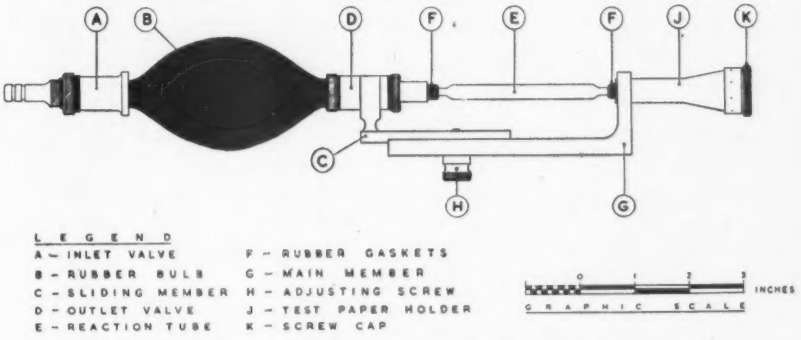

FIG. 1. *Diagram of apparatus for methyl bromide estimation.*

12 gm. of fuming sulphuric acid (56% free SO_3). Two and one-quarter inches of this filling are packed into 8 mm. diameter glass tubing under dry air conditions. The ends of the tubing are drawn out and sealed. The commercial mixture* called hoolamite (8) is of essentially the same composition.

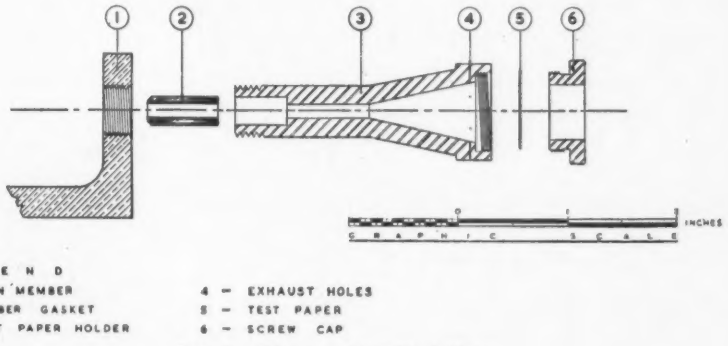

FIG. 2. *Diagram of test disc holder.*

Test discs are prepared from wax-ringed spot test paper** as developed by Yagoda (20). These are cut to outside diameter 1.75 cm. to fit the disc holder. For uniformity of response it is necessary to select papers having an inner diameter between 1.10 and 1.13 cm.

* *Mine Safety Appliance Company of Canada, Toronto.*
** *Carl Schleicher and Schuell #598Y.*

The color standard card, by means of which the concentrations of methyl bromide are estimated, contains 11 artificial color standards, arranged circularly on a cardboard square and overlaid by a circular rotatable cardboard disc perforated with a 1 cm. diameter hole by means of which one color at a time can be revealed. In the circular disc is a hole 18 mm. in diameter with microscope cover glass cemented in the bottom.* This well receives the test disc which is then masked by rotation of an oblong strip with a 1 cm. diameter hole. Opposite each color on the card the corresponding concentration (p.p.m.) of methyl bromide is marked.

The procedure in making a test with the instrument is as follows:

(*a*) The oxidation tube, tips broken off, is secured between the gaskets (F, Fig. 1) in the apparatus.

(*b*) With the apparatus in (or connected to) the atmosphere to be tested, the bulb is given 20 full squeezes, each being timed to four seconds (with one second for recovery of the bulb). This is necessary to establish equilibrium within the reaction tube.

(*c*) The test disc is inserted in the holder, 0.015 ml. fluorescein added to it by means of a capillary dropper, and seven squeezes (timed to four seconds) forced through.

(*d*) The test disc is removed at once, treated with one drop of sodium hydroxide solution, inserted in the well in the color card, masked, and matched within 45 sec.

(*e*) In subsequent trials 15 preliminary squeezes of test air through the reaction tube prior to inserting the test disc are sufficient to equilibrate the instrument. The reaction tube may be used until approximately one-third of the filling becomes discolored.

Calibration of Instrument and Effect of Lighting

Methyl bromide concentrations for calibration were prepared by adding measured amounts of liquid methyl bromide to a 2700 liter gas chamber. An alternative method was to add vapor to a 13 liter gas bottle equipped with a mechanical stirrer which it was found necessary to operate at high speed in order to avoid stratification and to secure a uniform mixture. Concentrations were routinely checked by the method of Williams (18).

As the colors produced on the test disc are not permanent it was necessary to prepare artificial color standards. The colors in color dictionaries such as that of Ridgway (14) were found to be too saturated for comparisons, but the system** of Plochere (13) was found to be ideal for the purpose. In this system which comprises 1248 oil-painted cards the composition of each color is given in terms of a set of pigments obtainable from the manufacturers. Thus the

* *Under the glass-bottomed well is a cardboard disc coated with a special "background color". See Tables I and II.*

** *This system was kindly brought to our attention and the final colors analyzed by Mr. W. E. K. Middleton of the National Research Council Ottawa.*

compositions of intermediate colors could be estimated and mixed, and those of the series of standards prepared in this way are given in Table I.

TABLE I

PIGMENT COMPOSITIONS OF COLOR CARD COLORS (INCANDESCENT LIGHTING)

Color as designated by the p.p.m. of MeBr in air represented by it	Composition of matching standard
0 p.p.m. MeBr	1 part brilliant green: 48 parts primrose yellow: 3250 parts white
10 " "	16 parts spectra yellow: 1 part spectra red: 2230 parts white
20 " "	1 part spectra yellow: 1 part spectra red: 394 parts white
30 " "	1 part spectra yellow: 2 parts spectra red: 518 parts white
40 " "	1 part spectra red: 194 parts white
50 " "	8 parts spectra red: 1 part spectra rose: 1170 parts white
60 " "	4 parts spectra red: 1 part spectra rose: 829 parts white
80 " "	2 parts spectra red: 1 part spectra rose: 408 parts white
100 " "	1 part spectra red: 1 part spectra rose: 342 parts white
150 " "	1 part spectra red: 2 parts spectra rose: 492 parts white
>150 " "	1 part spectra rose: 324 parts white
Background	4 parts spectra blue: 1 part monastral blue: 1680 parts white
All parts by volume	Pigments obtained from G. Plochere, Los Angeles, U.S.A. White is Luxor undercoat white, Canada Paint Company.

In order that the series of standards might be prepared from pigments other than those specified they were analyzed spectrophotometrically in terms of the I.C.I. standard observer and illuminant C (5, 7). The trichromatic coefficients x and y which designate the color were plotted and a smooth curve

TABLE II

SPECTROPHOTOMETRIC ANALYSIS OF COLOR CARD COLORS MATCHED TO TEST DISCS UNDER INCANDESCENT LIGHTING

Color as designated by concentration (p.p.m.) of MeBr in air it represents	Trichromatic coefficients		Relative brightness
	x	y	Y
0	.3453	.3930	78.96
10	.3551	.3689	78.21
20	.3605	.3380	71.88
30	.3549	.3351	67.22
40	.3480	.3240	67.07
50	.3570	.3189	60.55
60	.3522	.3130	61.22
80	.3559	.3043	56.01
100	.3525	.2985	55.32
150	.3522	.2930	54.30
>150	.3449	.2832	53.81
Background	.2841	.3016	85.80

drawn through the points. In this way a set of "improved" values of x and y, given in Table II, was obtained. The value of Y is also included in the table since it specifies the percentage reflectance of the sample (7, p. 9).

With the color card prepared as described, the instrument was given a series of trials with concentrations of methyl bromide ranging from zero to 150 p.p.m. to check the reproducibility of response. The results are shown in Fig. 3.

The matching of test discs to colored standards was performed under incandescent lighting. Wattage did not affect matching. Since the spectral compositions of the test disc and standard colors are different, it is to be expected that the matching would be altered by substituting other light sources of different spectral energies (2). Thus under a daylight fluorescent lamp test colors matched high by about 15% methyl bromide; under diffuse daylight

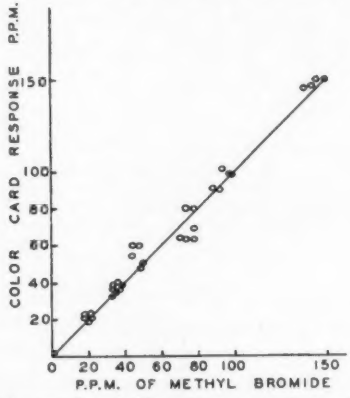

FIG. 3. *Typical plot of p.p.m. of methyl bromide versus color card response.*

response was also high by about 15% up to 80 p.p.m. and above that concentration matching was unsatisfactory; under a white fluorescent lamp response was normal, although matching was sometimes less exact. In view of these findings calibrations for use under incandescent and under diffuse daylight conditions are necessary. With either type, factors may be applied for the special lighting conditions as outlined above.

Effect of Other Factors

The iodine pentoxide–fuming sulphuric acid reaction mixture was found to give 100% oxidation of methyl bromide at 25°C., and 87% at −20°C. Thus there is substantially complete oxidation within the normal range of operation of the instrument. The effect of temperature on the test procedure was checked by carrying out two series of trials at 22°C. and 3°C. No difference in response greater than the accepted limits of accuracy of the test was found.

At humidities above 95% the reaction tube quickly becomes saturated with water and loses effectiveness. In such an event a small drying tube containing drierite was connected to the air inlet of the apparatus. It is advisable to employ the drying tube at humidities above 80% in order to prolong the life of the reaction tube. The passage of the test air through drierite had no effect on the response of the instrument.

Other brominated hydrocarbons which are oxidizable by the reaction mixture will naturally interfere with the methyl bromide test, but such interferences are not usually encountered. Interference by chlorinated compounds is evidenced by a more purple hue to the test disc. Thus, 100 p.p.m. of trichloroethylene and carbon tetrachloride did not interfere with the response for 50 p.p.m. of methyl bromide during the first trial, but the effect was cumulative and the interference was noted in succeeding trials with the same reaction tube. Iodine compounds do not interfere since the iodine is retained in the reaction tube. Petroleum fraction paint solvents if present in high concentration were found to reduce the intensity of the color reaction.

Under normal environmental conditions where temperature and humidity are not extreme and in the absence of the interfering substances referred to above, the accuracy of the results obtained by this method is mainly dependent upon control of the rate of squeezing the bulb, the confined area of the test disc, and the volume of fluorescein solution added to the test disc. In such circumstances methyl bromide concentrations ranging up to 150 p.p.m. in air can be estimated within $\pm$ 15% or $\pm$ 5 p.p.m., whichever is greater. The current status of toxicological limits for this substance is fluid and industrial health control, therefore, can be satisfactorily based on the analytical precision of the instrument.

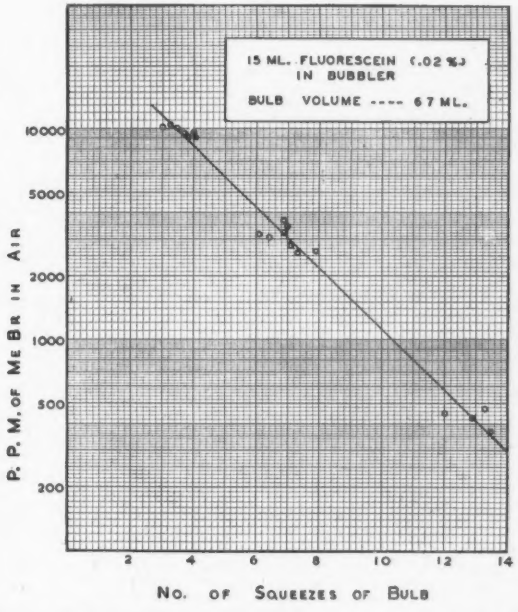

FIG. 4. *Plot of p.p.m. of methyl bromide versus volume of test air required to produce color change in fluorescein solution.*

High Concentrations of Methyl Bromide

It is often desirable to have a ready means of checking methyl bromide concentrations during fumigation, the concentration range in this case being approximately 500-10,000 p.p.m. It proved unfeasible to estimate such concentrations by the test disc method because the discs were either too intensely colored for visual matching or showed too little variation with concentration. Modification of the test method involved replacing the test disc by a small sintered glass bubbler connected to the reaction tube mixture by a short rubber tube. The bubbler contained 15 ml. of 0.02% fluorescein in 60% alcohol, the alcohol being necessary to prevent precipitation of the colored product formed. The instrument was calibrated against known gas concentrations by noting the number of squeezes (timed to four seconds per squeeze) before the liquid draining back down the sides of the tube turned from orange-yellow to pink. No addition of alkali was necessary, and the color change was sharp. The calibration curve is shown in Fig. 4. At these high concentrations 10 preliminary squeezes appeared to be sufficient to equilibrate the reaction tube but the tubes rapidly became exhausted, for after two trials at 10,000 p.p.m., response began to decrease.

Determination of Carbon Tetrachloride and Trichloroethylene in Air

According to Katz and Bloomfield (9), carbon tetrachloride does not interfere (i.e. produce discoloration in the reaction tube) in the detection of carbon monoxide by hoolamite. Nevertheless oxidation of both carbon monoxide and trichloroethylene to produce free chlorine does occur and 0.05% *o*-tolidine solution, which gives a yellow coloration with chlorine, was selected as the

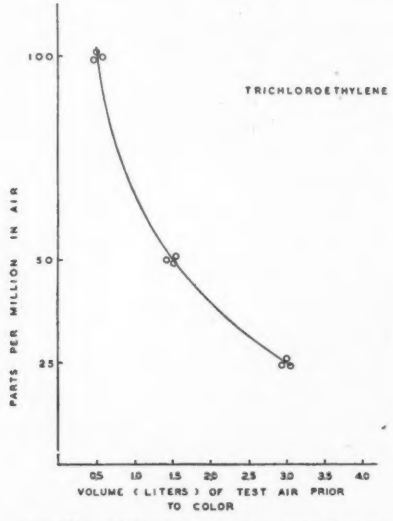

FIG. 5. *Plot of p.p.m. of trichloroethylene versus volume of test air prior to first detectable color on test disc.*

color producing reagent for the test disc. It is a sensitive reagent for chlorine (16) and was found to be reasonably stable to the sulphur trioxide fume from the reaction mixture. The wax-encircled discs were replaced by plain discs* and treated with 0.015 ml. of solution. Curves showing concentration vs. volume of air necessary to produce detectable color are given in Figs. 5 and 6.

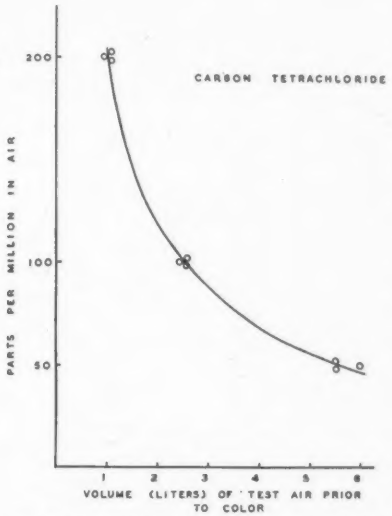

FIG. 6. *Plot of p.p.m. of carbon tetrachloride versus volume of test air prior to first detectable color on test disc.*

Occasionally the tube of reaction mixture became pale green throughout its entire length during the test and this phenomenon was almost invariably accompanied by low response. No explanation could be found for this behavior and such tubes were rejected as soon as green coloration was noted.

When trichloroethylene–air (or carbon tetrachloride – air) mixtures were forced through the iodine pentoxide – sulphuric acid reaction mixture, there was an initial period in which no detectable quantity of chlorine was evolved, although discoloration of the reaction mixture indicated that reaction was occurring. The volume of gas passed through the instrument before the first detectable color appeared on the test disc depended on the concentration of trichloroethylene in the air. After the first detectable color appeared the color intensity rapidly increased to a maximum which was more intense at higher concentrations. Following the development of color on the disc it was found that if air alone were passed through the instrument, there was a continued release of chlorine for a very long time as evidenced by strong coloration of fresh test discs. The test procedure was therefore based upon the volume of air

* *Cut from Carl Schleicher and Schuell, #598 ST spot test paper.*

necessary to produce first detectable color on the test disc. It is evident that each determination of a concentration of trichloroethylene (or carbon tetrachloride) requires a fresh tube of reaction mixture.

Large volumes were necessary to produce detectable color with air mixtures of these solvents. The apparatus was therefore modified as shown in Fig. 7.

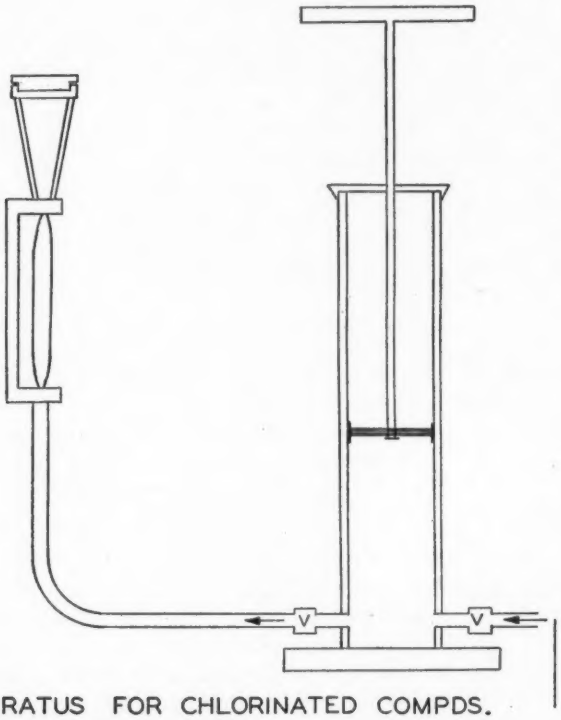

FIG. 7. *Diagram of apparatus for chlorinated hydrocarbon estimation.*

The pump was designed to deliver 500 ml. per stroke and the pumping rate timed to 35 ± 2 sec. per stroke.

Acknowledgment

The authors wish to acknowledge the assistance of Mr. T. F. Doherty in calibrating the instrument.

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A STUDY OF COLD-WATER SEPARATION OF BITUMEN FROM ALBERTA BITUMINOUS SAND ON A PILOT PLANT SCALE[1]

By L. E. Djingheuzian[2] and T. E. Warren[3]

Abstract

The cold-water method of separation of bitumen from bituminous sand consists basically in adding an oil diluent, water, an alkaline reagent, and a wetting agent to bituminous sand, disintegrating the mixture in a pebble mill, diluting with water, separating the major part of the sand in a classifier, and settling out water and finely divided inorganic matter in thickeners. The diluent is distilled from the oil product and recycled. This procedure was conducted in a pilot plant having a capacity of 200 to 300 lb. of bituminous sand per hour. Ore dressing machinery of standard design was used for all hydrometallurgical operations. Recovery of total oil was ordinarily about 97.5%, and the net recovery of bitumen, allowing for replacement of lost diluent, was about 95%.

Observations were made in the course of the pilot plant investigation on the effects of variation of alkaline reagents, temperature, diluent, wetting agents, ratio of water to bituminous sand, clay, and the properties of the bituminous sand charged.

Introduction

The bituminous sands of Northern Alberta are potentially a large source of liquid fuels, and areas of adequate extent and grade to support a major industry have been defined by drilling (5). The nature of the bitumen and its mode of occurrence, however, are such that commercial development will be feasible only after some complex technological problems have been solved. One of these is to devise a method for efficient and economic separation of bitumen from sand. At present, three methods are under consideration.

Of these, the one in the most advanced stage of development is the hot-water or McClave process (2) which has recently been demonstrated on a 500-ton-per-day scale by the Government of the Province of Alberta (1). The second method, employing the fluidized solids technique for distillation of oil from bituminous sand, has been investigated on a pilot plant scale by the National Research Council (9). Another investigation, conducted by the Mines Branch, has applied hydrometallurgical principles on a pilot plant scale to develop the cold-water separation method (11). The name derives from the fact that separation is carried out at 25°C. in contrast with the higher temperatures employed in the hot-water process.

The criteria that have guided the development of the cold-water process are as follows:

(1) it should recover a large proportion of the bitumen from the sand so as to reduce the costs of mining and handling per unit of bitumen produced;

[1] *Manuscript received in original form August 9, 1950, and, as revised, December 29, 1950. Contribution from the Canadian Chemical Conference, June, 1950, as Part II of a paper entitled, "A Proposed New Approach to the Development of the Alberta Bituminous Sands". Published by permission of the Director General of Scientific Services, Department of Mines and Technical Surveys, Ottawa.*

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(2) the fuel consumption for heat and power should be low, so that separation and refining steps can be carried by coke, obtained as a by-product from distillation of the separated bitumen;

(3) equipment should be simple and preferably of proven conventional design in order to reduce capital and operating charges;

(4) the process should not be so sensitive to changes in the composition of the bituminous sand as to limit the selection of sites for development;

(5) the contents of water and inorganic matter in the bitumen from the primary separation should be low so as to reduce the cost of subsequent operations.

The cold-water method was initiated in the laboratories of Abasand Oils, Limited, in 1944, and a large scale unit was installed in the Horse River plant of that company in 1945. This unit gave such good results that the entire plant was converted so as to employ the cold-water procedure. Before operation on this scale was begun, however, the plant was destroyed by fire. Records of the experimental work were lost, and separation operations of the Abasand Company were discontinued. Since 1945 studies of the cold-water method have been carried on by the Mines Branch, first on a laboratory scale and later in a small pilot plant.

Laboratory Research (10)

The laboratory-scale experiments were applied to a study of the basic principles of the method. Briefly, it consists in adding a light oil diluent, an alkaline reagent, and water to bituminous sand; the mixture is subjected to a disintegrating operation in a ball mill and after addition of more water is agitated and allowed to settle. The oil recovered by this procedure at temperatures around 25°C. is about 98% of the total bitumen and diluent charged. In the laboratory experiments, the effects of hydrogen ion concentration, alkaline reagents, temperature, and clay concentration were investigated.

In preliminary tests, distilled water was used without the addition of an alkaline reagent. At the end of the separation procedure the water had a pH value of about 8.0 and the recovery of bitumen was only about 75%. In later experiments alkaline reagents were used, in quantities equivalent to 1 or 2 lb. of reagent per ton of bituminous sand, which raised the pH of the water to the range between 9.0 and 11.5 and resulted in higher recoveries of bitumen. Variations within this range did not influence the recovery.

From six alkaline reagents tried, sodium silicate, sodium carbonate, and sodium hydroxide gave markedly better results than lime, caustic starch (starch produced by boiling starch paste in a dilute solution of sodium hydroxide) and alum. A further series of experiments made for the purpose of comparing the first three reagents yielded the data shown in Table I. With all three reagents, the unrecovered bitumen in the sand tailings was less than 2% of the total, and it is apparent, therefore, that under the conditions of the experiments they can be considered to be about equally effective.

TABLE I

Reagent	Unrecovered bitumen in sand tailings as % of bitumen charged
Sodium silicate	1.5
Sodium carbonate	0.9
Sodium hydroxide	1.9

When clay was added to the charge of bituminous sand to simulate conditions in other parts of the field, the effect of the three alkaline reagents was as shown in Table II. It is apparent from Table II that, in the presence of clay, sodium silicate was less effective than the other two reagents.

TABLE II

Reagent	Recovery of bitumen and diluent, %			
	No clay	10% clay	20% clay	30% clay
Sodium silicate	97.9	92.8	....	93.3
Sodium carbonate	98.4	95.2	91.9	94.9
Sodium hydroxide	97.6	96.8	94.8	93.9

The effect of temperature on recovery is shown in Table III. In the experiments the bituminous sand, water, apparatus, and ambient air were maintained at the indicated temperatures.

In the early laboratory experiments the presence of clay resulted in a cleaner primary sand but increased the amount of oil carried down with the fine solids that settled later. In order to investigate this effect, a series of runs was made

TABLE III

Temperature, °C.	Number of tests	Recovery of bitumen and diluent, %
10	3	92.9
15	5	97.1
21	13	97.7
27	3	98.3
32	3	98.5

using 5, 10, and 15% of clay as an addition to the bituminous sand. Both the bituminous sand and clay used in these experiments were selected from drill-core samples from the Steepbank area. The results, shown in Table IV, confirm the observation that better separation is obtained if clay is present in quantities less than 15% of the bituminous sand.

TABLE IV

Clay added to feed, %	Number of tests	Temperature, °C.	Recovery of bitumen and diluent, %
0	1	21	97.7
5	5	21	98.4
10	5	21	98.1
15	2	21	97.6

Pilot Plant Investigations

Having established a procedure by which high recoveries of bitumen could be obtained, it appeared advisable to test it further in a small pilot plant equipped with standard ore-dressing machinery. The purpose of the pilot plant investigation was to work out a flow sheet and operating technique that could be made the basis for large scale operation.

The designed capacity of the pilot plant was based upon a feed rate of 200 lb. of bituminous sand per hour. The initial arrangement of machinery comprised a low-discharge pebble mill, 2 ft. in diameter and 3 ft. long, an agitator, a rotary classifier, two cone classifiers, and two settling tanks. Transfer of materials was by vertical centrifugal pumps. The complete plant also included equipment for final dehydration, diluent recovery, and coking, but this is not dealt with in the present paper which is concerned only with the hydrometallurgical part of the procedure.

The bituminous sand used for the preliminary tests was from the Horse River property of Abasand Oils, Limited, near McMurray. This sand is more firmly consolidated than that occurring further north and the bitumen in it is more viscous.

The operational procedure was developed by about twenty preliminary runs. Staff was not available for shift operation, and it was found convenient to make daily runs of about five hours' duration. In general, an operating period of five hours was too short to reach a steady-state condition and maintain it for a satisfactory test period. With each change of apparatus, material, or procedure, it became the practice, therefore, to maintain operation for five of the five-hour period. Sampling and analysis were on a daily basis.

The preliminary runs indicated that four distinct steps are needed to recover a large proportion of the bitumen in the form of an oil with low enough contents of water and inorganic matter to be acceptable for the subsequent distillation. These steps are as follows:

(1) Mixing and disintegration of the charge of bituminous sand, water, diluent, and reagents. The weight of water in the mixture is about one-third that of the bituminous sand; the weight of diluent is about equal to that of the bitumen in the sand.

(2) Addition of water to the mixed and disintegrated charge and agitation to liberate bitumen and diluent from sand. The weight of water added was approximately two and a half times that of the charge of bituminous sand.

(3) Classification of agitator discharge into sand and oil slurry fractions.

(4) Settling of the oil slurry to remove water and finely divided inorganic matter.

The temperature was not adjusted to suit the individual operations and was approximately constant throughout the separation procedure. In the preliminary runs, the optimum temperature appeared to be between 23° and 27°C. Below 23°C. the separation was incomplete and at temperatures of 28°C. and higher free oil was discharged with the sand tailings from the classifier.

In experiments employing the initial apparatus and procedure indicated recoveries of oil were about 97%, and the oil product from the top of the settling tank after 16 to 20 hr. of settling had an average composition of 76.4% oil, 1.9% mineral matter, and 21.7% water. There was, however, a loss of oil in the sludge that accumulated in the bottom of the settling tanks The magnitude of this loss was not known at first and it was not taken into consideration in calculating the recovery of oil. In the final arrangement of apparatus, a different settling procedure eliminated sludge formation.

During the preliminary runs, the equipment was progressively altered and the final apparatus and operating scheme were as follows. The low-discharge pebble mill was satisfactory, as initially used for the mixing and disintegration step. With a charge of 0.5 lb. of pebbles per lb. of bituminous sand per hour, the oil was separated with very little size reduction of the sand. The agitator was also satisfactory. The vertical centrifugal pumps were found to cause froth formation and were replaced by suction pumps with a positive action. The rotary classifier was replaced by a 14 in. by 8 ft. duplex rake classifier. The settling operation was carried out in two thickeners. The classifier overflow was pumped into the first of these, which was 4 ft. in diameter and 4 ft. deep. The overflow from the first thickener was the finished product of the hydrometallurgical section of the plant. The underflow from the first thickener, which still carried appreciable amounts of oil, was pumped to a second thickener 4 ft. in diameter and 3 ft. deep. The underflow from the second thickener was sent to waste and the overflow returned to the first thickener. The settling tanks were removed in order to avoid prolonged settling which was always attended by sludge formation. The revised flow sheet is shown in Fig. 1.

The combination of apparatus shown in Fig. 1 eliminated the necessity of settling the thickener overflow but complicated the reduction of water and inorganic matter contents of the product to permissible limits. Later experimental work was, therefore, largely directed towards development of a procedure that would produce an oil containing less than 30% of water and not more than 5% of inorganic solids.

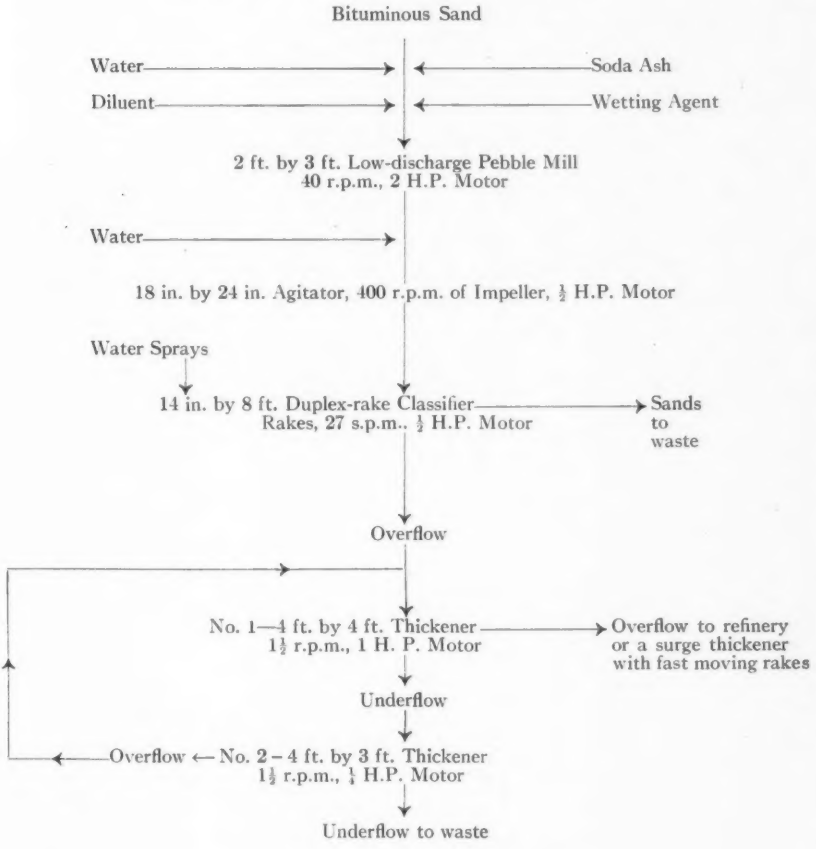
Bituminous Sand
Water
Soda Ash
Diluent
Wetting Agent
2 ft. by 3 ft. Low-discharge Pebble Mill
40 r.p.m., 2 H.P. Motor
Water
18 in. by 24 in. Agitator, 400 r.p.m. of Impeller, ½ H.P. Motor
Water Sprays
14 in. by 8 ft. Duplex-rake Classifier
Rakes, 27 s.p.m.. ½ H.P. Motor
Sands to waste
Overflow
No. 1—4 ft. by 4 ft. Thickener
1½ r.p.m., 1 H. P. Motor
Overflow to refinery or a surge thickener with fast moving rakes
Underflow
Overflow ← No. 2 – 4 ft. by 3 ft. Thickener
1½ r.p.m., ¼ H.P. Motor
Underflow to waste

FIG. 1. *Final flow sheet.*

Observations from Experimental Data with a Study of Operating Variables

The terms used in discussion of the experimental data are defined as follows:

Diluent—a distillate from petroleum or bitumen added to the charge to reduce the specific gravity and viscosity of the bitumen;

Oil—combined bitumen and diluent;

Crude oil or finished product—No. 1 thickener overflow;

Classifier sands—inorganic solids eliminated by classifier.

Tails—No. 2 thickener underflow;

Total tails—Classifier sands + No. 2 thickener underflow;

Classifier extraction—oil overflown by the classifier and pumped into No. 1 thickener;

Recovery—oil overflown by No. 1 thickener and delivered to the refinery;

Net recovery—bitumen input minus total oil loss in terms of bitumen.

Hence:

$$\% \text{ sands eliminated by classifier} = \frac{\text{classifier sands, lb.}}{\text{inorganic solids in feed, lb.}} \times 100$$

$$\% \text{ classifier extraction} = \frac{\text{oil input} - \text{oil in classifier sands}}{\text{oil input}} \times 100$$

$$\% \text{ indicated recovery} = \frac{\text{oil input} - \text{oil in total tails}}{\text{oil input}} \times 100$$

$$\% \text{ net recovery} = \frac{\text{bitumen input} - \text{oil in total tails}}{\text{bitumen input}} \times 100.$$

(*a*) *Alkaline Reagents and pH*

Three alkaline reagents, sodium carbonate, sodium silicate, and sodium hydroxide, were tested in the pilot plant. Of these, sodium silicate did not produce as good recoveries as soda ash, probably because of the presence of clay. The use of sodium hydroxide was discontinued because it appeared to cause emulsification, as indicated by the brown color of the crude oil. Commercial grade sodium carbonate (soda ash) was, therefore, used as the alkaline reagent for most of the experiments.

Table V shows the effect of variations in the quantity of soda ash and the consequent variation in pH upon the indicated recovery of oil.

TABLE V

	Test No.				
	1	2	3	4	5
Number of daily runs	2	5	5	5	4
Bituminous sand feed, lb./hr.	155	223.5	215.1	233.0	225.0
Bitumen input, lb./ton of feed	307	318	328	303	290
Diluent (kerosene) input, lb./ton of feed	307	352	340	312	308
Wetting agent (Span 80) lb./ton of feed	Nil	0.062	0.062	0.047	Nil
Soda ash, lb./ton of feed	*Nil*	*Nil*	*1.18*	*1.31*	*2.0*
pH of classifier overflow	...	*8.1*	*8.8*	*9.5*	*9.8*
Temperature of classifier overflow, °C.	25	25.5	24.4	26.0	25.2
Loss of bitumen, lb./ton of feed	29.0	19.5	13.1	8.8	8.7
Loss of diluent, lb./ton of feed	29.0	21.5	13.5	9.1	9.2
Indicated recovery of oil, %	*90.7*	*93.9*	*96.1*	*97.1*	*97.0*

From Table V it will be observed that:

(1) when no soda ash was used, the indicated recovery of oil was at its lowest, namely, 90.7%,

(2) when no soda ash was used, but a wetting agent (Span 80) was added, the recoveries improved more than 3%,

(3) when small amounts of soda ash were used with Span 80, the indicated recovery improved still further. In the presence of the wetting agent, with pH values of 8.1, 8.8, and 9.5, recoveries were 93.9, 96.1, and 97.1% respectively,

(4) when large amounts of soda ash were used without the wetting agent and the pH was 9.8, the recovery was maintained at 97%.

In general, these observations confirm the laboratory tests and give further evidence that the pH in the mill circuit should not be less than 9.

(*b*) *Temperature*

In the laboratory experiments the influence of temperature on recovery of oil had been studied in the range between 10° and 32°C. A continuing increase in recovery had been observed up to the highest temperature although the rate of increase was low at temperatures above 21°C. For this reason most of the runs in the pilot plant were conducted at 25°C., and no systematic study of the temperature variable was made. Occasional irregularities in temperature control made it possible, however, to observe the influence of temperature over a comparatively narrow range.

No runs of acceptable precision were made at temperatures below 24°C., but in a few brief periods of operation at lower temperatures separation of bitumen from sand appeared visually to be incomplete, confirming the laboratory experiments. At higher temperatures, however, some controlled runs were made when the water supply to the plant was unusually warm. The results of two comparable series of runs at different temperatures, using kerosene as diluent, are given in Table VI.

TABLE VI

	Series I	Series II
Number of daily mill runs	5	5
Rate of feed, lb. bituminous sand/hr.	231	220
Total oil input, lb./ton of feed	666	667
" " " , lb./hr.	76.9	73.4
Average temperature, °C.	*24.7*	*28.6*
" pH	9.4	9.6
Oil entrained in classifier sands, %	0.43	0.66
Extraction of oil by classifier, %	*98.8*	*97.9*

In Table VII are shown four comparable runs, in one of which the average temperature was 30.5°C. These runs were made with Bitumount diluent, which was much more viscous than kerosene.

The data in Tables VI and VII indicate that at temperatures exceeding 28°C. classifier extractions decrease. This was confirmed by visual observation of the classifier sand which appeared to contain free oil at the higher temperatures. The fact that the change in diluent, with the consequent change in vis-

TABLE VII

	Run No.			
	1	2	3	4
Rate of feed, lb. bituminous sand/hr.	233	234	210	216
Total oil input, lb./ton of feed	666	614	668	681
" " " , lb./hr.	77.5	71.8	70.1	73.5
Average temperature, °C.	25.9	27.9	27.2	30.5
Average pH	9.0	9.1	9.0	9.0
Oil entrained in classifier sands, %	0.2	0.2	0.2	0.9
Extraction of oil by classifier, %	99.4	99.4	99.4	97.3

cosity of the oil, did not alter the temperature effect suggests that it is not due to the influence of temperature on viscosity.

(*c*) *Diluent*

The function of diluent is to combine with the bitumen, decreasing its viscosity, so that it can be separated from the sand, and decreasing its specific gravity so that it rises to the surface of water. The diluent is added before the mixing and disintegration step and passes through the hydrometallurgical procedure along with the bitumen. The bitumen–diluent mixture is then distilled and, in the complete cycle, the volatile fraction is returned to the mixing and disintegration step. Since the process should be independent of extraneous sources of diluent, losses incurred in the circuit must be made up from the bitumen. If these losses are large the make-up diluent must include high-boiling fractions of the bitumen. Under steady-state conditions, therefore, the properties of the diluent are a function of the proportion of diluent lost.

In the pilot plant experiments diluent losses were about 3%, so that 3% make-up would be required per cycle. If loss and replacement were continued long enough, therefore, the diluent would consist of the most volatile 3% of the bitumen, which has a specific gravity approximating that of kerosene.

It was not feasible, in the present experiments, to continue recycling long enough to approach constant diluent composition. If losses of diluent were replaced intermittently, the percentage of initial diluent in the circuit after n cycles would be 100 (0.97^n). Reduction of the proportion of initial diluent to 10% would, therefore, require 76 cycles. Taking one of the five-hour daily runs as a convenient period for accumulation and recovery of diluent, 76 days or 380 hr. of operation would be required. The proportion of initial diluent would decrease faster if the losses were replaced continuously. In this case, the amount of initial diluent remaining in the circuit after θ hours of operation is given by the equation,

$$D_I = D_T e^{-\frac{A\theta}{D_T}}$$

in which D_I and D_T are the amounts of initial and total diluent, and A is the rate of replacement. Assigning values of $D_T =$ 100 lb. and A = 1 lb. per hour,

the initial diluent would be 10% of the total after 230 hr. Even this time, however, is too long for experiments in which frequent changes of conditions are necessary.

The pilot plant experiments were conducted, therefore, with extraneous diluents of constant composition. The first of these to be used and the one employed for most of the tests was commercial kerosene. The other was a fraction with a relatively high final boiling point that was distilled from bitumen at the Bitumount plant of the Alberta Oil Sands project. Diluents evolved in operation of the complete cycle of the cold water procedure will probably have properties between those of kerosene and the Bitumount distillate. Table VIII lists some of the properties of the two diluents.

TABLE VIII

	Diluents	
	Kerosene	Bitumount*
Specific gravity at 60°F.	0.809	0.883
Viscosity, Saybolt universal seconds		
at 70°F.		47.9
at 100°F.		40.2
Sulphur, % by weight		1.90
Water, % by volume (A.S.T.M.)		0.2
Distillation		
Initial boiling point, °F.	330	147
End point, °F.	540	572**
Residuum, % by volume	1.8***	2.7

* *The Bitumount diluent, as received, had a low flash point and contained hydrogen sulphide. It was, therefore, treated with caustic soda and blown with air before use.*
** *At pressure of 40 mm. of mercury.*
*** *Includes distillation loss.*

No systematic study was made of the effect of varying the ratio of bitumen to diluent. This was ordinarily about 50:50 on a weight basis. In one series of runs, however, the proportion was changed to 62.7:37.3 which gave an indication of the effect of increasing the bitumen:diluent ratio.

Table IX shows the results of comparable series of runs made with each diluent, and with an increased ratio of bitumen:diluent.

The results with the Bitumount diluent were not significantly different from those with kerosene. Increase in the bitumen:diluent ratio did not greatly affect classifier extractions or indicated recoveries, but lowered the amount of inorganic matter eliminated by the classifier and increased the contents of water and inorganic matter in the finished product.

(*d*) *Wetting Agents*

In the laboratory experiments and preliminary runs with the pilot plant, no wetting agent was used. Later, however, the settling step was altered by re-

TABLE IX

Test number	1	2	3	4
Number of daily runs	5	5	5	3
Bituminous sand feed, lb./hr.	238	216	300	266
Bitumen content of sand, % by weight	15.8	16.5	14.9	16.5
Diluent	*Kerosene*	*Bitumount*	*Kerosene*	*Kerosene*
Ratio of bitumen to diluent, by weight	*51.2: 48.8*	*49.0: 51.0*	*48.3: 51.7*	*62.7: 37.3*
Soda ash, lb./ton of feed	1.46	0.89	1.56	1.46
Wetting agent (Span 80), lb./ton of feed	0.041	0.041	0.031	0.038
pH of classifier overflow	9.5	9.0	9.3	9.3
Sand eliminated by classifier, %	92.8	92.3	88.3	83.8
Extraction of oil by classifier, %	98.6	99.0	98.8	98.7
Indicated recovery of oil, %	97.8	97.5	97.7	96.9
Thickener overflow:				
Oil, %	71.3	70.9	75.6	50.5
Inorganic matter, %	2.1	2.7	2.2	5.2
Water, %	26.6	26.4	22.2	44.3

placing the cone classifiers and settling tanks with thickeners. This alteration resulted in increased proportions of water and inorganic solids in the finished product.

To assist water wetting of solids and coalescing of the water droplets and thus to improve settling, experiments were started with wetting agents.

After preliminary tests with a commercial detergent (Dreft) laboratory experiments were conducted with about 60 wetting agents from which Span 80*, Span 40*, and Rosin Amine D Acetate** were selected for use in the pilot plant.

Two other factors, soda ash concentration and aeration influenced the purity of the finished product and these must be taken into consideration in the study of wetting agents. The degree of aeration is affected by the type of pump used to transfer the oil slurries. When vertical centrifugal pumps were replaced by suction pumps, aeration was greatly reduced.

Table X shows the effect of wetting agents on classifier extraction, indicated oil recovery, and grade of oil produced when kerosene was used as diluent and vertical centrifugal pumps for transfer of oil slurries.

The quantity of wetting agent used was based on the amount of water added to the pebble-mill feed. From the laboratory investigation it appeared that the correct quantity of wetting agent was 0.041 lb. per ton of bituminous sand charged. In one of the tests shown in Table XI, the rate of charging was 300 lb. per hour which altered the amount of water in proportion. The amount of wetting agent, however, was not increased so that it was 0.031 lb. per ton of

Manufactured by the Atlas Powder Co., Wilmington, Del.
**Manufactured by the Hercules Powder Co., Wilmington, Del.*

TABLE X

No. of runs	Feed rate, lb./hr.	Bitumen content, %	Oil input, lb./hr.	Soda ash, lb./ton	pH of C.O.F.*	*Wetting Agent*, lb./ton	Classifier extraction, %	Indicated recovery, %	No. 1 thickener overflow		
									% oil	% M.M.**	% water
5	225	15.5	69.5	2.0	9.7	None	99.1	97.2	62.2	2.5	35.3
5	225	16.2	71.8	2.0	9.6	*Dreft*, 0.5	98.7	96.7	68.0	2.2	29.8
5	231	16.8	76.7	2.0	9.4	*Aerosol O.T.*, 0.12	98.8	96.6	53.7	4.4	41.9
5	224	15.9	72.4	None	8.1	*Span 80*, 0.062	98.6	93.9	55.3	5.1	39.6
5	215	16.4	70.5	1.18	8.8	*Span 80*, 0.062	98.7	96.1	67.8	5.9	26.3
5	232	16.6	76.6	1.09	8.9	*Rosine Amine D*, 0.058	98.3	96.5	69.5	2.5	28.0
5	233	15.2	73.6	1.31	9.5	*Span 80*, 0.047	98.2	97.1	62.9	4.3	32.8

*C.O.F. = *classifier overflow.*
**M.M. = *mineral matter.*

TABLE XI

No. of runs	Feed rate, lb./hr.	Bitumen content, %	Oil input, lb./hr.	Soda ash, lb./ton	pH of C.O.F.	*Wetting agent*, lb./ton	Classifier extraction, %	Indicated recovery, %	No. 1 thickener overflow		
									% oil	% M.M.	% water
5	238	15.8	74.3	1.46	9.5	*Span 80*, 0.041	98.6	97.8	71.3	2.1	26.6
4	238	16.2	75.0	1.45	9.2	*Rosin Amine D*, 0.041	98.6	97.1	71.5	1.3	27.2
5	300	14.9	92.4	1.56	9.3	*Span 80*, 0.031	98.8	97.7	75.6	2.2	22.2
3	215	15.9	67.5	1.51	9.1	*Span 40*, 0.041	99.3	98.2	75.6	1.7	22.7

bituminous sand. The change in concentration of wetting agent did not influence the recovery but improved the grade of the thickener overflow.

Table XII shows the effect of wetting agents with Bitumount diluent and suction pumps.

Laboratory tests had indicated that less soda ash was required with Bitumount diluent than with kerosene and the amount used in the first series of runs in Table XII was as determined by the laboratory. The pH in this series, however, was below 9 and a greater amount of soda ash was used in subsequent runs.

TABLE XII

No. of runs	Feed rate, lb./hr.	Bitumen content, %	Oil input, lb./hr.	Soda ash, lb./ton	pH of C.O.F.	*Wetting agent*, lb./ton	Classifier extraction, %	Indicated recovery, %	No. 1 thickener overflow		
									% Oil	% M.M.	% water
5	170	15.4	52.0	0.68	8.6	*Span 80*, 0.062	99.2	96.5	67.5	3.0	29.5
5	216	16.5	72.6	0.89	9.0	*Span 80*, 0.041	99.0	97.5	70.9	2.7	26.4

The conditions of the runs shown in Table XII were similar to those of the first series, shown in Table XI. The results were also practically the same. The Bitumount diluent used in the second series had a higher specific gravity and viscosity than those of kerosene so that it appears that the effect of the wetting agent must have been greater in the second series with the Bitumount diluent.

Reviewing the experiments with wetting agents, their effect on classifier extraction and indicated recovery was negligible and their principal effect was in improvement of the grade of the thickener overflow. Of the three wetting agents, Span 40 was slightly the best, followed by Span 80 and Rosin Amine D Acetate. Before a final selection is made, however, it is advisable to conduct further tests over longer periods of time. The final selection will have to be based on economic as well as technical factors. The cost of the wetting agent, however, is not a major item of expense; with the agents used, it is in the order of one cent per ton of bituminous sand separated.

(*e*) *Water*

The amount of water required for the whole separation procedure was not studied systematically prior to the pilot plant tests. A preliminary run indicated that the weights of water added to the pebble mill and agitator should be, respectively, one-third and three times the weight of the charge of bituminous sand. Most of the pilot plant runs were carried out with ratios of total water to feed between 5: 1 and 3.5: 1. Variations were due to irregularity in the supply of water to the agitator and wash sprays of the classifier. Within these limits, changes in the ratio of water to charge did not influence the results.

When a heat balance applying to large scale operation in the field was prepared, it indicated that a major proportion of the total heat requirement of the process would be needed to raise the temperature of the river water supplied to the plant to 25°C. It was, therefore, considered advisable to determine the minimum quantity of water that could be used for efficient separation. Three pilot plant runs were made for this purpose with varying ratios of total water to charge, keeping other conditions constant. Table XIII is an analysis of water additions for each of these runs.

TABLE XIII

	Run No. 1	Run No. 2	Run No. 3
Bituminous sands treated, lb.	1140	1140	1140
Water content of classifier sands, lb.	271	298	295
Water content of No. 1 thickener overflow, lb.	107	95	91
Water content of No. 2 thickener underflow, lb.	3055	2606	1735
Total water in the circuit, lb.	3433	2999	2121
Less, moisture content of bituminous sands, lb.	8	11	13
Total water added to the circuit, lb.	3425	2988	2108
Water added to the pebble mill, lb.	361	361	350
Water added to the agitator, lb.	1485	1389	1063
Water in classifier sprays (by difference), lb.	1579	1238	695
Ratio, pebble-mill water: feed	0.3: 1	0.3: 1	0.3: 1
agitator water: feed	1.3: 1	1.2: 1	0.9: 1
classifier water: feed	1.4: 1	1.1: 1	0.6: 1
total water: feed	3.0: 1	2.6: 1	1.8: 1

Table XIV shows the results obtained in the three runs with varying ratios of water to bituminous sand feed, together with those of a previous series of runs made under comparable conditions.

From Table XIV it can be seen that reduction of the total water added to the circuit reduced the recovery of oil. For the highest recovery of oil it is necessary to use a ratio of total water to bituminous sand feed of 3: 1 or higher. In all runs with reduced ratios the grade of the thickener overflow was satis-

TABLE XIV

	Previous series	Run No. 1	Run No. 2	Run No. 3
Feed rate, lb./hr.	215	226	226	233
Bitumen content, %	15.9	15.5	14.4	15.4
Ratio of bitumen to kerosene	50.8: 49.2	49.3: 50.7	47.5: 52.5	49.9: 50.1
Oil input, lb./hr.	67.5	71.0	68.6	72.0
Soda ash, lb./ton	1.51	2.0	2.0	2.0
Span 40, lb./ton	0.041	0.041	0.041	0.041
Temperature of classifier overflow, °C.	25.0	25.3	24.8	24.6
pH of classifier overflow	9.1	8.5	8.4	8.3
Ratio of added water to feed	*3.5: 1*	*3: 1*	*2.6: 1*	*1.8: 1*
Classifier extraction, %	99.3	99.1	99.3	98.1
Indicated recovery, %	98.2	98.2	97.1	96.6
No. 1 thickener overflow: oil, %	75.6	75.2	76.6	75.7
M.M., %	1.7	2.1	1.8	4.0
water, %	22.7	22.7	21.6	20.3

factory but at the lowest ratio the inorganic solid content of the thickener overflow was about double that of the higher ratios. Further reduction in the water: feed ratio would probably have produced an oil with too great a content of inorganic solids to be acceptable for the subsequent distillation. An economic balance will have to be made in order to determine the optimum ratio but this will probably be between 2.5: 1 and 2: 1.

In Table XIV it will be observed that, although higher amounts of soda ash were used in Runs 1 to 3 than in the previous series, the pH values were lower. Runs 1 to 3 were made several months after the previous series and it is considered possible that the lower pH value may have been due to some chemical change in the sample of bituminous sand.

(*f*) *Clay as a Factor Causing Oil Loss*

It had been found in the laboratory experiments that the presence of clay improved the separation of bitumen from sand but that large amounts of clay reduced the recovery of oil. These observations were similar to those of Clark and Pasternack, applying to the hot-water separation process (3). The mechanism by which clay affects the cold-water separation procedure is, however, very complex and it was considered advisable to make observations on clay during the course of the pilot plant runs. It was not expected that the pilot plant study would lead to a rigorous explanation of the mechanism, but it was hoped to gain enough insight into it to direct the course of a more thorough investigation.

In previous work clay has usually been estimated by measurement of the range of particle size. This method is, of course, unreliable in the presence of finely divided sand. In the present work, therefore, clay was estimated chemically by determining the aluminium oxide content of the sample and multiplying it by a factor of 3. The clay contents of the pebble-mill discharge and the classifier overflow were determined in this way. If, in addition to these analyses it is assumed that the inorganic matter in the thickener overflow is entirely clay, the amount of clay in the classifier underflow and thickener underflow can be calculated. Operating with Horse River sand the clay contents of the inorganic matter of the pebble-mill discharge and classifier overflow were between 4 and 7%, and 33 and 39% respectively.

Table XV summarizes the effects of clay on classifier extraction and No. 2 thickener overflow.

From a study of Table XV, four conclusions can be drawn:

(1) As the clay content of the feed increases from 4.1 to 4.8%, classifier extractions increase from 98.6 to 99.3%. Extractions appear independent of oil viscosity and wetting agent.
(2) The ratio of oil to clay in the tails (No. 2 thickener underflow) was approximately constant with each diluent and wetting agent.
(3) Wetting agents appeared to influence the ratio of oil to clay in the thickener underflow. The lowest ratio was obtained with Span 40 and the highest with Rosin Amine D Acetate.
(4) Increase in oil viscosity increases the ratio of oil to clay in the thickener underflow.

Examination of the sludge that is formed by settling of the thickener overflow also contributes to the data relating to the effect of clay on oil losses. Prolonged settling is not essential to the cold-water separation procedure but

TABLE XV

Series of runs	Bituminous sands feed, lb.	Clay in feed, lb.	Clay in feed, %	Ratio of bitumen to diluent in mill feed	Viscosity of oil, centi-poises	*Wetting agent* used	Classifier extrac-action, %	Loss of oil in tails, lb.	Clay in tails, lb.	Oil loss per lb. of clay lb.	Oil loss in tails per ton of feed, lb.	Recovery of oil by thick-from C.O.F., %	Indi-cated re-covery, %
Mill runs with kerosene													
1	6,550	269.3	4.1	51.2:48.8	103.7	*Span 80*	98.6	17.6	175.6	0.100	5.4	99.1	97.8
2	4,050	165.8	4.1	51.4:48.8	103.7	*Rosin Amine D Acetate*	98.6	18.5	112.3	0.165	9.1	98.5	97.1
3	6,600	281.2	4.3	48.3:51.7	103.7	*Span 80*	98.8	22.0	197.1	0.112	6.7	98.9	97.7
4	4,150	175.0	4.2	62.7:37.3	....	*Span 80*	98.7	19.8	120.9	0.164	9.1	98.2	96.9
5	3,110	149.4	4.8	50.8:49.2	103.7	*Span 40*	99.3	10.1	167.8	0.060	6.5	99.0	98.2
Mill runs with Bitumount diluent													
6	4,450	195.7	4.4	50.4:49.6	336	*Span 80*	99.2	35.6	169.2	0.210	16.0	97.4	96.5
7	5,700	233.7	4.1	49.0:51.0	336	*Span 80*	99.0	27.3	106.3	0.257	9.6	98.6	97.5

in the earlier pilot plant runs it was employed in order to produce oil with low contents of water and mineral matter.

The amount of oil in the resulting sludge is indicated in the oil balances shown in Tables XVI and XVII.

TABLE XVI

CUMULATIVE OIL BALANCE FOR 33 RUNS WITH KEROSENE DILUENT

	Pounds	Per cent of total oil charged
Pure oil recovered	11,211.0	87.23
Oil in samples, (6 lb./run, estimated)	198.0	1.54
Oil in sludge	*768.4*	*5.98*
Oil in total tails	387.9	3.02
Assumed oil losses due to evaporation, accidental losses, and discrepancies in sampling and analysis	286.8	2.23
Total indicated input of bitumen + diluent based on daily samples of bituminous sand and measured additions of diluent	12,852.1	100.00

Comparison of the ratio of oil to clay in the sludge with that in the thickener underflow affords some evidence on the influence of particle diameter on the amount of oil retained by clay. A sample of sludge, after repeated stirring to liberate free oil, reached a stable ratio of 0.82 lb. of oil per lb. of clay. The comparable ratio in the thickener underflow was about 0.1 lb. of oil per lb. of clay. The average particle diameter of the clay in the thickener underflow was

TABLE XVII

CUMULATIVE OIL BALANCE FOR 10 RUNS WITH BITUMOUNT DILUENT

	Pounds	Per cent of total oil charged
Pure oil recovered	2800.1	85.51
Oil in samples (6 lb./run, estimated)	60.0	1.83
Oil in sludge	*320.1*	*9.78*
Oil in total tails	94.4	2.88
Total indicated input of bitumen + diluent based on daily samples of bituminous sand and measured additions of diluent	3274.6	100.00

estimated by consideration of settling rates to be 5 to 10 times that of the clay in the sludge. The amount of oil retained per unit weight of clay appears, therefore, to be inversely proportional to the particle diameter of the clay or directly proportional to its specific surface.

The observations on clay made in the course of the pilot plant runs indicate that, under the conditions of operation that have been developed, clay has an

important influence on oil loss. The pilot plant apparatus and procedure, however, are not suitable for a study of the fundamental reactions involved. Laboratory-scale research into the mechanism of association of bitumen with the types of clay occurring in the field is needed in order to interpret reliably the results observed in the pilot plant and to indicate how its operation can be improved.

It is suggested that the research begin with a determination of the types of clay most prevalent in the field. With this information available it may be possible to postulate a mechanism for the retention of bitumen by clay. The structures of various clays have been established by Pauling (8), Hofmann, Endell, and Wilm (4), and others, and are reviewed by Marshall (7). Some clays, notably the bentonites, have a laminar lattice that is expansible in one direction. Such clays are organophilic owing to base exchange of cations situated between the layers of the lattice, with organic cations, and are capable of a high degree of swelling in the presence of organic solvents (6). The swelling takes place in only one dimension and exchange of ions and adsorption of organic molecules must take place along the edges of the lattice. The rate of adsorption is thus increased by increase in area of the exposed edge resulting from reduction of the size of the clay particles. At present, such a mechanism is speculative but it gives an indication of the nature of the investigation that might be made into the influence of clay on oil losses.

(g) *Test with Bituminous Sand from Bitumount*

Most of the pilot plant runs were made with bituminous sand from the Horse River area but in order to test the cold water method with bituminous sand having different properties, a series of runs was also made with a sample from Bitumount. The operating conditions and results of 10 runs with the Bitumount sample, using kerosene as diluent and Span 40 as wetting agent are shown in Table XVIII. Data from a similar series of runs with Horse River bituminous sand and the same diluent and wetting agent are also shown in Table XVIII for comparison.

Data in Table XVIII show that, under similar operating conditions, oil losses with Bitumount sand are higher than those with Horse River sand. The conditions employed were those that had been found best for separation of the Horse River sand, because the Bitumount sample was not large enough to permit an experimental search for optimum conditions. With different operating conditions the recovery of oil might have been improved, but it is also possible that the higher losses are inherent in the different nature of the clay and bitumen in the Bitumount sample.

The latter view is supported by the following observations:

(1) The erratic values of pH observed during the runs with Bitumount sand indicated that the clay varied greatly in amount and/or composition.
(2) The oil loss per pound of clay with the Bitumount sand was 10 times as high as that with the Horse River sand.

TABLE XVIII

	Bitumount sands	Horse River sands
Bituminous sands treated, lb.	11,070	3,110
Rate of feed, lb./hr.	231.3	215.0
Bitumen content, %	15.1	15.9
Clay content, %	6.6	4.8
Soda ash, lb./ton	2.50	1.51
Span 40, lb./ton	0.047	0.041
Average temperature, °C.	25.1	25.0
Average pH of classifier overflow	9.5	9.1
Variations of pH	8.7 to 11.7	9.05 to 9.2
Ratio of bitumen to kerosene in feed	49.3:50.7	50.8:49.2
Viscosity of oil, centipoises at 21°C.	31.4	103.7
Specific gravity of oil at 21°C.	0.895	0.915
M.M. eliminated by classifier, %	85.5	82.0
Oil entrained in classifier wet sands, %	0.45	0.26
Classifier wet sands, lb.	10,450	2,811
Classifier extraction, %	98.6	99.3
Oil in classifier overflow, lb.	3341.1	974.8
Clay in classifier overflow, lb.	295.5	189.5
Oil in No. 2 thickener underflow (tails), %	0.32	0.10
No. 2 thickener underflow to waste, lb.	38,280	10,120
Loss of oil in No. 2 thickener underflow, lb.	120.6	10.1
Clay in No. 2 thickener underflow, lb.	190.7	167.8
Oil loss per lb. of clay, lb.	0.63	0.06
Oil loss per ton of feed, lb.	21.8	6.5
Recovery of oil by thickeners from classifier overflow, %	96.4	99.0
Indicated recovery, %	95.0	98.2
No. 1 thickener overflow: oil, %	80.4	75.6
M.M., %	2.6	1.7
water, %	17.0	22.7

(3) The lower viscosity of the bitumen–diluent mixture indicated that the bitumen from the Bitumount sample differed in physical properties from that of the Horse River sample.

(4) The thickener overflow with the Bitumount sand contained more clay and less water than that with the Horse River sand.

(5) The sample of bituminous sand from Bitumount had a higher clay content than is usual for that area, though it was this high clay content that prompted the mill runs with Bitumount sand. Results obtained on this particular sample, therefore, would not necessarily apply to the deposit as a whole.

Summary and Conclusions

A continuous procedure based on the cold-water method for separation of bitumen from bituminous sand has been developed on a pilot plant scale. As applied to bituminous sand from the Horse River area the procedure gave a net recovery of bitumen, allowing for replacement of diluent, of 95%. The net recovery from bituminous sand from the Bitumount area was 90%. The recovered oil had water and inorganic matter contents of about 25 and 2.5% respectively. Methods for dehydration, diluent recovery, and coking were developed but are not described in the present paper.

The hydrometallurgical procedure was carried out in four successive steps, namely, disintegration, agitation, classification, and thickening. Ore-dressing equipment of standard design was employed for all four steps.

Chemical factors in the procedure were studied and the following conclusions reached: use of an alkaline agent is imperative and soda ash was the most effective of those tested; the pH of the classifier overflow should be greater than 9; the optimum temperature range is between 23 and 27°C.; use of wetting agents improved oil recoveries and reduced water and inorganic matter contents of the thickener overflow; the optimum water to bituminous sand ratio was 3: 1 but economic considerations may lead to use a ratio as low as 1.8 to 1 in commercial practice; the presence of clay improved separation in the classifier but reduced recovery in the thickener so that there appears to be an optimum clay concentration for highest over-all recovery; the mechanism by which clay influences the procedure appears to be complex and requires further research of a fundamental nature.

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DYNAMIC ADSORPTION OF AMMONIA, OF BUTANE, OF CYANOGEN CHLORIDE, AND OF WATER VAPOR BY CHARCOALS[1]

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Abstract

A balance and accessory apparatus was designed for continuously determining the weight of gas or vapor removed from an air stream by a porous adsorbent. This apparatus was used to evaluate the dynamic adsorption of ammonia and of butane on a steam activated, coconut shell charcoal, and also the dynamic adsorption of cyanogen chloride and of water on steam activated coconut shell charcoal; on steam activated, copper impregnated, coal and wood charcoal; and on steam activated, copper and chromium impregnated, nutshell charcoal. In general, the results obeyed present day theories as shown by: the distribution of the adsorbed gases through the adsorbate bed; the adsorption isotherms; and the effect of such factors as adsorbate concentration and mass flow rate on break time. Measurements of the rate and amount of temperature rise during the adsorption of butane by coconut shell charcoal were related to measurements of changes in the adsorption wave. Calculations of the areas of coconut shell charcoal covered by the different compounds at various partial pressures indicated that ammonia was adsorbed as a gaseous film, that butane was adsorbed as a monomolecular layer, that cyanogen chloride was adsorbed in a manner intermediate to these, and that water was adsorbed by capillary condensation.

Introduction

Porous adsorbents are used industrially for recovery of solvents or gasoline, purification of gases, removal of odors, dehydration of air, and other processes in which a readily adsorbable vapor is mixed with a carrier gas that is less readily adsorbed (6). A suitable adsorbent should have the ability to adsorb selectively the gas to be removed, a high rate of adsorption, a large adsorption capacity, chemical stability to the mixture of gases, mechanical strength, low flow resistance, and usually should permit ready recovery of the adsorbate. Common adsorbants are charcoal for gases and hydrocarbon vapors, and alumina or silica gel for water vapor. The mixture of gases and vapors is passed through the adsorbent bed: the unsaturated layers of adsorbent nearest to the entrance remove most of the vapor from the stream until they approach saturation, then the site of adsorption moves progressively towards the exit end of the bed (adsorption wave). The heat of adsorption is liberated at the site of

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adsorption and is distributed between the carrier gas and the adsorbent. The capacity and the efficiency of the adsorbent decrease as the temperature rises. Studies of the physics of dynamic adsorption have resulted in many theories and equations to explain this process (5, 8, 9, 10, 15, 16, 19).

A saturated adsorbent is usually regenerated and the adsorbate may sometimes be recovered. This desorption is done by heating, evacuating, blowing with steam, or passing a stream of hot inert gas through the bed. The process of desorption has also received theoretical treatment (3, 19).

The value of theories may be determined by performance tests which show the effect of the various factors involved. This paper describes a large capacity adsorption balance which was used to measure the effect of variations in the concentration of adsorbate in the carrier gas, of different velocities through the adsorbent bed, of moisture content, and of the nature and depth of some charcoals on the dynamic adsorption of ammonia, butane, cyanogen chloride, and water vapor.

Materials and Analytical Methods

Table I gives a description and some characteristics of the steam activated charcoals used.

TABLE I

DESCRIPTION AND SOME CHARACTERISTICS OF THE STEAM ACTIVATED CHARCOALS USED IN THIS STUDY

Designation and description	Volume activity*	Grading** and shape of granule	Moisture saturation value,*** %
A. Coconut shell charcoal (trace of silver)	20.5	8–20 mesh flat chips	37.9
B. Copper impregnated coal and wood charcoal	17.1	8–20 mesh round grains	28.7
C. Chromium impregnated nutshell charcoal	23.0	14–32 mesh grains	36.8

* *Standard carbon tetrachloride test, values supplied by the maker.*
** *Mesh sizes refer to standard Canadian grading.*
*** *Calculated on the dry weight of the sample.*

The anhydrous ammonia, as received from Canadian Industries Limited, and the butane, as received from the Ohio Chemical and Manufacturing Co., were passed into the system through drying towers. The cyanogen chloride was prepared by suspending reagent grade sodium cyanide in carbon tetrachloride and treating it with chlorine in a freezing bath. The cyanogen chloride was separated from the mixture by distillation and purified by repeated recrystallizations until a freezing point of −6.90°C. was obtained. The purity of the recrystallized material was better than 99.9%.

Ammonia in the effluent carrier gas (air) was determined by passing a sample through a sulphuric acid scrubber and determining excess acid.

Butane in the effluent carrier gas was determined by the combustion of a sample and evaluating butane by the volume change or by passing the contents of the sample tube through a combustion tube at 1000°C. and into standard sodium hydroxide.

Cyanogen chloride was detected in the effluent stream by the appearance of a yellow color in 50 ml. of a 0.5 *M* solution of sodium hydroxide containing 1.25 gm. of pyridine. The stream was then switched to an alternate set of absorption towers and the process repeated to give continuous absorption of the effluent vapor. The pyridine solution was acidified with 5 ml. of concentrated nitric acid and left standing at room temperature. The liberated chloride was titrated with 0.02 *M* mercuric nitrate using sodium nitroprusside as an indicator.

Adsorption System

The portion of the system preceding the adsorption cell is shown diagrammatically in Fig. 1A. Air from a pump was passed through a filter (not shown) to remove oil and smoke, and then into a 45,000 cc. ballast reservoir, A, with a blowoff, B. After passing through three sulphuric acid bubblers represented by C, the air passed through a series of soda-lime tubes, D, to remove carbon dioxide, through a series of calcium chloride tubes, E, to remove moisture, and then was brought to any desired moisture level in a series of sulphuric acid–water bubblers, F. A scratched stopcock, I, permitted close control of the volume of air admitted to the cell at X. The rate of air flow was measured by a calibrated butyl phthalate manometer, G, and checked with a wet test meter

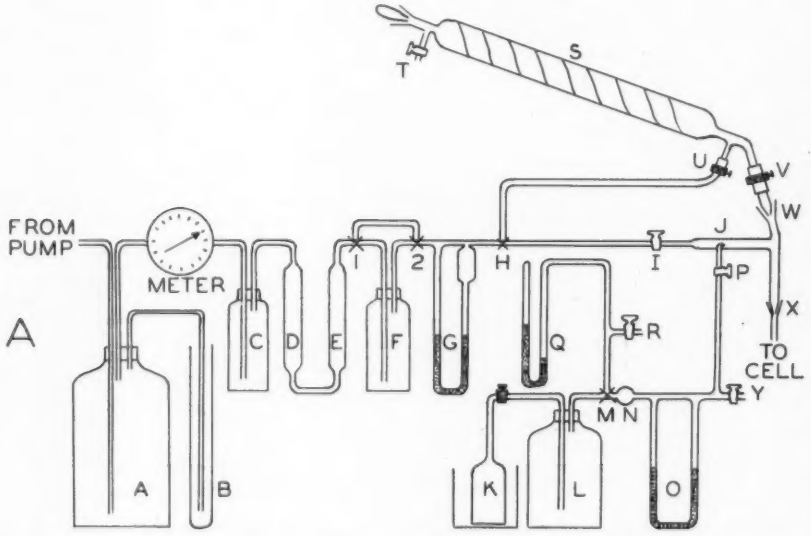


FIG. 1A. *The adsorption system: Portion preceding the adsorption cell.*

filled with butyl phthalate. The exhaust, H, also led to a calcium chloride tube which was used to check the moisture content of the air before a determination was begun. When in operation, air was carried directly to the cell at J and adsorbate was admitted to the air at this point.

The adsorbate was admitted from a cylinder or flask at K to a 26,280 cc. storage volume, L. The pressure in L was measured by a mercury manometer, Q. By maintaining the pressure in L above atmospheric and by careful regulation of a scratched stopcock, P (or a needle valve), the adsorbate was admitted to the air stream at any desired rate. The bulb, N, provided a ballast volume and O was a calibrated manometer. The release, Y, permitted regulation of the adsorbate flow to the desired value before its introduction into the air stream. When necessary this system was evacuated at R.

The adsorbent was stored in the vessel, S, and prior to use was conditioned by heating to 400 ± 10°C. for 12 hr. in a stream of dry carbon dioxide-free air. After conditioning, the adsorbent was allowed to cool to room temperature and, by diverting the air stream through H, U, and T, was brought into equilibrium with air at the desired moisture content for another 12 hr. The screw clamp and rubber tubing at V permitted delivery of the required amount of charcoal into the cell without exposure to anything but air of the desired moisture content. Packing of the adsorbent was believed to be constant, since this arrangement delivered the charcoal from a constant height. The stopcocks U and T, on the conditioner, were kept closed except when conditioning was taking place. The rubber tubing, V and U, permitted rotation of the storage vessel when charcoal delivery into the cell was necessary.

Fig. 1B shows an adsorption cell (A to D) that was satisfactory, and shows one method of sampling the effluent air stream (E to K). The adsorption cell consisted of a piece of glass tubing 21 cm. long, with an inside diameter of 4 cm. A brass cap was fastened to the top of the tube with DeKhotinsky cement. Through the center of the cap a brass tube 1.5 cm. in inside diameter and 7 cm. long penetrated into the adsorption cell. The walls of this tube were 0.25 mm. thick. The bottom of the cell was closed by a similar cap, the only difference being that the tube extended out of, rather than into, the cell. This bottom cap was attached to a brass ring by a semiscrew arrangement of projections, D, in the brass ring and by slits in the cap. This permitted the cap to be drawn tightly against the bottom of the tube, and permitted ready access to the interior of the cell. The brass ring was also fastened to the glass tubing with DeKhotinsky cement. The brass tubes dipped into cups, B and B_1, filled with butyl phthalate or light hydrocarbon oil and attached to the inlet tube and outlet tubes (these sealing materials were varied with different adsorbates to eliminate any adsorption at this part of the system). This effectively sealed the cell and permitted it to move freely.

The adsorbent rested on a piece of metal gauze which was attached to a very short length of glass tubing, arranged to allow the air to flow freely out of the

cell. The cell depth was marked in centimeters, zero being gauze level, which permitted ready estimation of the depth of adsorbent up to 6 cm.

The cell was suspended from the arm of a balance by two light chains or fine wires attached to pivots in a ring, A, which clamped around the cell. This arrangement permitted an accuracy in weighing of about ± 0.005 gm. in earlier models and ± 0.002 gm. in later designs.

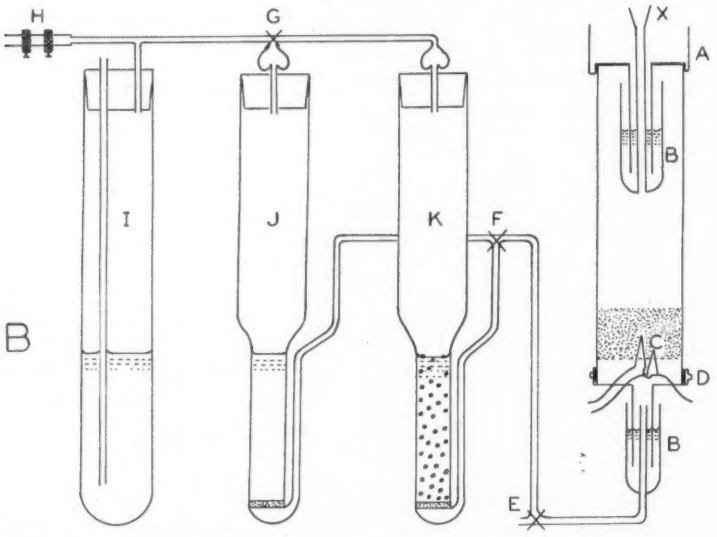


FIG. 1B. *The adsorption system: The adsorption cell and some apparatus for analyzing the effluent gas stream.*

In earlier models, one thermocouple, C, was in the center of the cell and the other was 1.5 cm. away from it. Both were 0.5 cm. above the metal gauze supporting the adsorbent. This arrangement permitted measurement of the temperatures in the lowest centimeter layer of the charcoal bed. In later models, the temperature was measured at points, in the center of the charcoal bed, which were 1.2 and 2.5 cm. from the exit end. The thermocouples wires were B & S No. 28 gauge, coiled loosely, and did not interfere with the accuracy of the weighing.

In the earlier models, samples of the air leaving the adsorption cell were collected in evacuated gas pipettes of about 600 cc. capacity, attached through a capillary tube at E (Fig. 1B). The capillary tube allowed the pipettes to be filled at a rate smaller than the flow rate of the air stream, thereby preventing room air from being drawn into the bulb. In later models, provision was made for analysis of the effluent stream by sucking it through stopcocks F and G into sintered disc bubblers (Fig. 1B). By adjusting H and I, the suction was

made equal to the air flow through the cell, thus avoiding any effect on the ring seals. By these sampling methods, at least 95% of any unadsorbed adsorbate was accounted for in each trial.

The system was enclosed in a cabinet at a temperature of 23° ± 1°C. throughout the experiment.

Adsorption Procedure

A dried, carbon dioxide-free air stream was passed through the calcium chloride tube at a known rate for a definite length of time to determine the moisture content. (In dry charcoal experiments the air contained about 0.004% water vapor by volume.) When a satisfactory moisture content was obtained, the air was passed through the cell to remove any traces of moisture that might have collected. The empty cell was weighed with the air flow momentarily deflected through H (Fig. 1A). Flow was recommenced through the cell and the required amount of charcoal delivered. The charcoal weight was then taken, with the air stream again deflected. Finally, the cell was balanced in the presence of the air stream, and temperature equilibrium was attained.

The rate of flow of adsorbate was regulated using the blowoff, Y (Fig. 1A), and at the appropriate moment the adsorbate flow was directed into the air stream and the pressure on the manometer, O (Fig. 1A), was recorded. Weight increments were generally determined at five minute intervals and were determined at three minute intervals when a 1-cm. charcoal bed was used. Temperature readings were taken more frequently. Samples of issuing gas were taken whenever the time was believed appropriate, which could be determined reasonably well from the thermocouple readings. When the adsorbent was saturated, increment in weight of the charcoal was determined in the absence of the gas–air stream, as a check on readings taken in its presence. The maximum differences in these two sets of weighings was ± 0.02 gm.

Adsorption of Ammonia, Butane, and Cyanogen Chloride

For the work described here, dry gases were used and air was the carrier gas. Ammonia and butane adsorption was studied using dry coconut shell charcoal, and cyanogen chloride adsorption was studied using the three charcoals (coconut shell, impregnated coal and wood, and impregnated nutshell) in the dry state.

Fig. 2 shows changes in weight of the adsorbent (or volume of gas adsorbed) as a function of time. The amount adsorbed increases linearly with time until the break-through time (break time) is reached. The slope of this linear portion depended on the rate of supply of adsorbate (Fig. 2A) and was independent of the air flow rate (Fig. 2B). The graphical representation masks the accompanying desorption of air from the charcoal. The initial portion of the line is not in reality straight but slightly concave toward the time axis because of the weight of the air displaced. The actual average gain in weight shown on

the curves in the linear portion is thus slightly less than the amount of adsorbate taken up. The desorption of air is detectable only at the higher concentrations where the loss in weight amounts to about 5% of the weight adsorbed. Despite repeated efforts to evaluate this effect more accurately, its

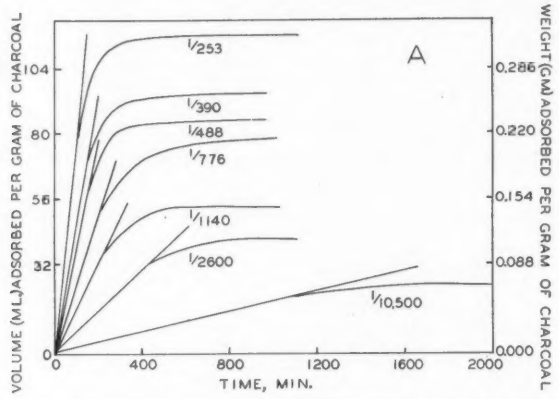
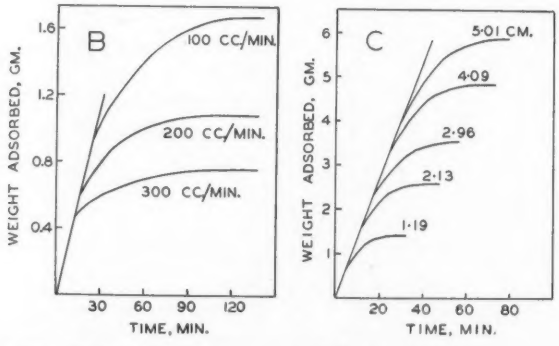


FIG. 2A. *Weight increases in coconut shell charcoal beds: Effect of changing the cyanogen chloride concentration in air as carrier gas flowing at 500 cm. per min. through 5-cm. adsorbent bed.*



FIGS. 2B and 2C. *Weight increases in coconut shell charcoal beds:*
B. Effect of changing air flow rate on the adsorption of ammonia (flow rate, 60 cc. per min.) by a 5-cm. adsorbent bed.
C. Effect of changing the bed depth on the adsorption of butane (flow rate, 53 cc. per min.) from air stream (flow rate, 1530 cc. per min.).

magnitude was within the limits of error of the analytical methods and only an estimate could be made. Desorption of air occurs at the beginning of the adsorption process and is almost complete at the time (break time) when the adsorbate starts to appear in the effluent stream. Fig. 2C shows the increase in break time and in total weight of adsorbate taken up (equilibrium or saturation weight) with increase in depth of the charcoal bed.

The experimentally determined curves for various bed depths makes possible the calculation of distribution of the adsorbate in a column (3). Fig. 3A shows the distribution of butane throughout a 5-cm. charcoal bed when the adsorbate flow was 53 cc. per min. and the air flow was 1530 cc. per min. The

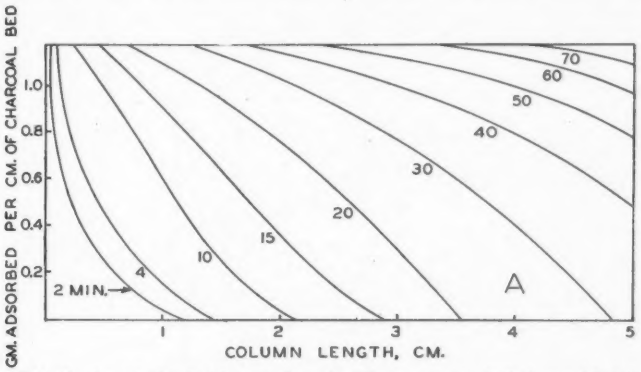
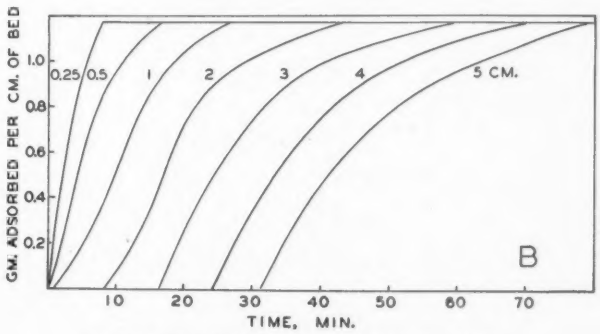


FIG. 3. *Distribution of adsorbed butane through a 5-cm. coconut shell charcoal bed (butane flow rate, 53 cc. per min.; air flow rate, 1530 cc. per min.).*
A. Change in distribution through the bed with time.



B. Amount adsorbed in any level at various times.

shapes of the various curves are in general agreement with theoretical predictions (3, 15, 16). The curves for two and four minutes follow the exponential form postulated, but curves for longer times show retardation in adopting an exponential form of distribution at the top of the column. This retardation has been attributed to filling of the larger capillaries in the adsorbent and to slow migration of material adsorbed on the surface into inner capillaries. Another possible factor may be the time required to remove the heat of adsorption, which increases the temperature of the charcoal and thereby reduces the amount of gas adsorbed until some cooling has occurred.

Fig. 3B, developed from Fig. 3A, shows the weight of butane adsorbed plotted against time, for different depths of charcoal bed. The relation between

the weight adsorbed and time appeared to follow a relation postulated elsewhere (18),

$$X = W(1 - e^{-bt})$$

where X is the weight of gas adsorbed in time, t, W is the equilibrium weight of the gas adsorbed, and b is a constant.

Fig. 4 shows that distribution of cyanogen chloride through coconut shell charcoal was similar to the distribution shown during initial stages of butane adsorption by this adsorbent. However, the other charcoals retarded the penetration of small quantities of this gas and the normal distribution was obtained only after break-through of the adsorbate.

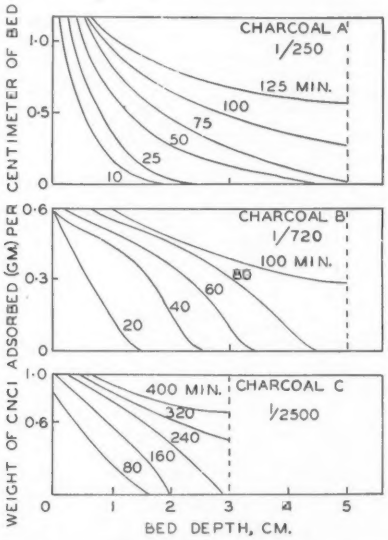


FIG. 4. *Distribution of adsorbed cyanogen chloride through coconut shell (A), impregnated coal and wood (B), and impregnated nutshell (C) charcoals (adsorbate concentration shown on graphs as fraction of total gas concentration; mass flow rate, 500 cm. per min.).*

If adsorption was continued to complete saturation of the charcoal bed, equilibrium weight adsorbed varied with air flow rate or adsorbate flow rate (Fig. 5), and with depth of the charcoal bed (Fig. 6). The time to reach saturation was greater proportionally for shallow beds than for deep beds (Fig. 7). This was due to rapid saturation at these depths as compared with the time required to dissipate heat generated by adsorption.

Equilibrium weights adsorbed are a function of an adsorption isotherm for dynamic systems. The equilibrium values obtained are a particular balance between the relative adsorption capacity of the charcoal for the adsorbate and the relatively inert carrier gas. They were not rigorously determined in this apparatus but they are indicative of the trend for any adsorbate – adsorbent – carrier gas combination. At equilibrium with a particular adsorbate concen-

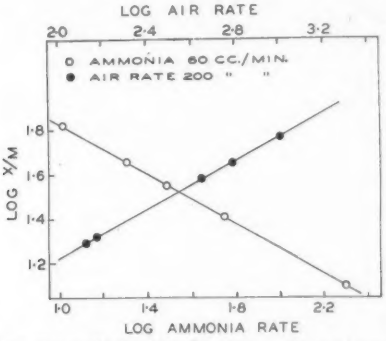


FIG. 5. *Effect of air flow rate and adsorbate flow rate on the total amount of ammonia adsorbed by coconut shell charcoal* $\left(\frac{x}{m} = \text{cc. adsorbate per gm. adsorbent}\right)$.

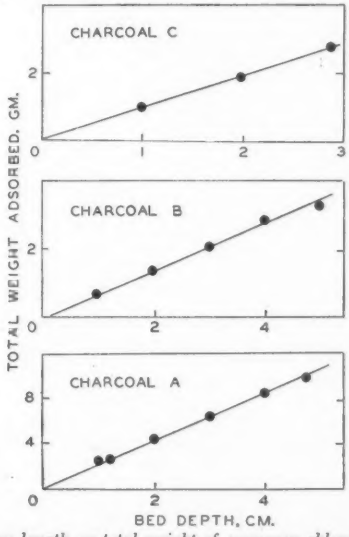


FIG. 6. *Effect of column length on total weight of cyanogen chloride taken up by coconut shell (A), impregnated coal and wood (B), and impregnated nutshell (C) charcoals (mass flow rate, 500 cm. per min.; adsorbate concentrations,* $\frac{1}{2500}$ *for C,* $\frac{1}{720}$ *for B, and* $\frac{1}{253}$ *for A).*

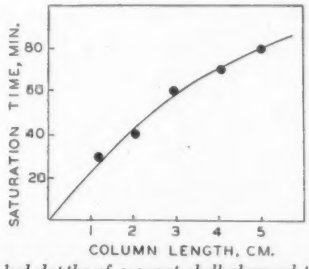


FIG. 7. *Time for various bed depths of coconut shell charcoal to become saturated with butane (butane flow rate, 53 cc. per min.; air flow rate 1530 cc. per min.).*

tration, the measured increase in weight was lower than the true weight of adsorbate taken up, since some air was desorbed from the adsorbent. This error in the weight adsorbed was within the limits of accuracy claimed. Determination of the adsorption isotherm for dynamic systems is as important as isotherms for static systems, since it provides a general characterization of results such as those presented in Figs. 2, 5, and 6. Because of possible channelling through the absorbent bed, isotherms for dynamic systems would be vitiated by the use of mass flow rates (carrier gas plus adsorbate) that exceeded the limitations of the adsorbent bed. In the adsorption system described in Fig. 1, the mass flow rate was kept below 3500 cc. per min. and no difficulties were encountered.

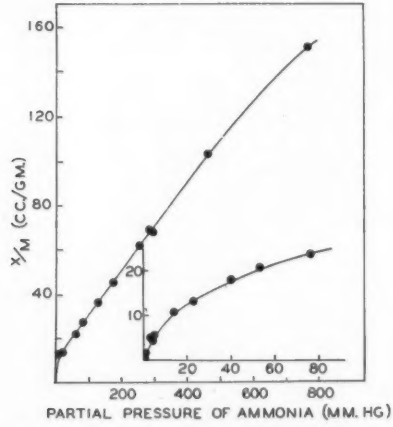


FIG. 8. *Dynamic adsorption isotherm of ammonia on coconut shell charcoal.*

The adsorption isotherm for ammonia on coconut shell charcoal (Fig. 8),

$$\frac{x}{m} = 1.05\ P^{0.764}$$

where $\frac{x}{m}$ represents cc. of ammonia absorbed per gram of charcoal and P represents the partial pressure of ammonia in millimeters of mercury, held fairly well for partial pressures above 50 mm. A better empirical representation was

$$\frac{x}{m} = \frac{0.278P}{1 + 0.00055P}$$

The almost linear relation apparent in this isotherm, above a relative pressure of about 0.02, has also been found in isotherms for hydrogen cyanide and cyanogen chloride on charcoal (6).

On one lot of cocoanut shell charcoal, the butane adsorption isotherm (Fig. 9) was

$$\frac{x}{m} = 42.6\ P^{0.146}$$

where $\frac{x}{m}$ represents cc. of butane absorbed per gram of charcoal and P represents the partial pressure of butane in millimeters of mercury. While this relation held at partial pressures up to 80 mm., it did not give a good value for 760 mm. pressure of butane, which was observed by experiment to be 89.2 cc. per gram. For another lot of coconut shell charcoal, the adsorption isotherm was

$$\frac{x}{m} = 33.0\ P^{0.13}$$

between 0 and 50 mm. partial pressure of butane.

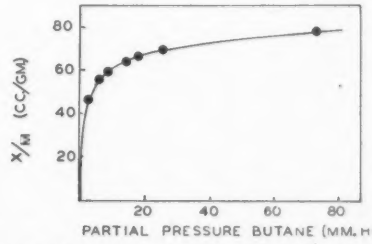


FIG. 9. *Dynamic adsorption isotherm of butane on coconut shell charcoal.*

The dynamic adsorption isotherms for cyanogen chloride on coconut shell and on impregnated coal and wood charcoals are compared in Fig. 10 with those determined elsewhere for a coal charcoal (3). The adsorption isotherms are:

for coconut shell charcoal $\frac{x}{m} = 4.68\ C^{0.488}$

for impregnated coal and wood charcoal $\frac{x}{m} = 2.37\ C^{0.477}$

where $\frac{x}{m}$ represents grams of cyanogen chloride per gram of charcoal and C represents the mole fraction of the adsorbate or $\frac{p}{p + p_0}$ where p is the partial pressure of the gas.

The shape of the curve showing the amount of adsorbate emerging from the effluent face of the cell may be found by determining the amount adsorbed per minute from the weight–time curve or by direct determination of the effluent concentration itself (both of these methods have been used in this work). The

results for two different bed depths are plotted in Fig. 11A. These curves may be symmetric or asymmetric depending on whether adsorption is a single physical process or involves several mechanisms.

Examination of the curves showing the amount escaping and the amount adsorbed per minute in Fig. 11A shows that the increase in weight of the cell was not as great as the product of the influent concentration and the time.

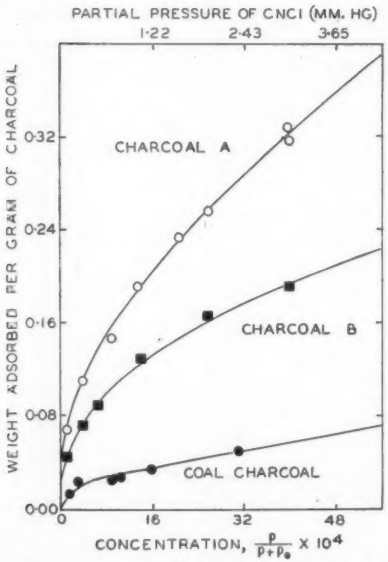


FIG. 10. *Dynamic adsorption isotherm of cyanogen chloride on coconut shell (A), on impregnated coal and wood (B), and on a coal charcoal (P is the partial pressure of the gas).*

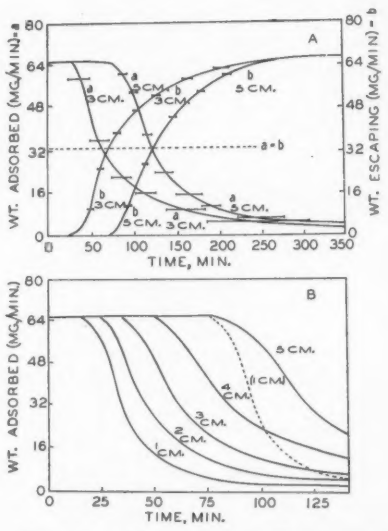


FIG. 11. *Adsorption and effluent curves showing change with time of the amount of adsorbate (supplied at 68 mgm. per min.) taken up per unit time.*
A. Discrepancy due to desorption of air.
B. Effect of depth of the adsorbent bed.

This discrepancy was caused by the desorption of air. Its magnitude has been slightly emphasized in this figure, but, in practice, it is within the limits of error in determining the amount escaping per minute in the effluent stream.

When plotted for different bed depths, these curves show how the shape of the adsorption wave changes as it moves through the bed (Fig. 11B). The curves for effluent concentration do not acquire a constant shape at various bed depths and show that the amount adsorbed after the break time is much less for the shorter bed depths. To make the comparison of the slopes for different bed depths more obvious the broken line marked 1 cm. is the curve for that bed depth moved along the time axis until the break time coincides with the break time for a 5 cm. bed. Since the effluent rate curves are almost the mirror image of these curves, the slope of the effluent rate versus time curves will decrease as the bed depth increases.

The effluent curves after adsorption of cyanogen chloride on charcoal are asymmetric, and the asymmetry increases with a decrease in initial concentration of the adsorbate (Fig. 12). The asymmetric form may be understood if the mechanism of the initial process is such as to result in the irreversible adsorption of the gas while the later portion is a reversible physical adsorption.

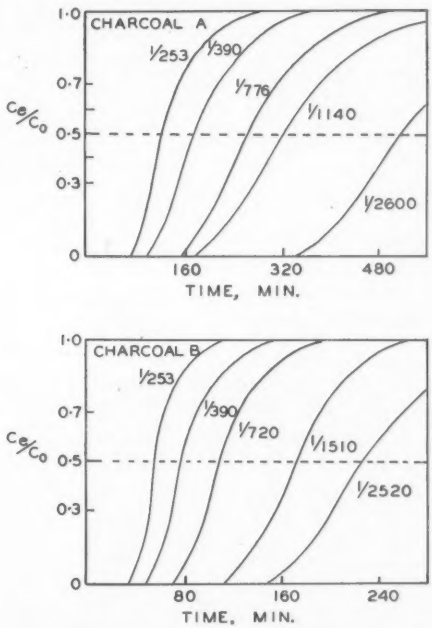


FIG. 12. *Effluent concentration curves for the adsorption by coconut shell (A) and impregnated coal and wood (B) charcoal (bed depth, 5 cm.) of cyanogen chloride at different concentrations in an air stream (mass flow rate 500 cm. per min.).*

From the position of the mid-point of these effluent–concentration–time curves in the time axis the rate of motion of the adsorption wave through the bed may be determined. The average rate of advance of the adsorption wave was 0.043 cm. per min. for a concentration of 1/253 of cyanogen chloride in air on coconut shell charcoal and 0.045 cm. per min. for a concentration of 1/720 of cyanogen chloride in air on impregnated coal and wood charcoal. The rates are approximately constant for any one charcoal and the distance along the bed over which the wave is distributed increases with increasing bed depth.

It has been shown by theory (8) that

$$\ln(C_0/C - 1) = -kC_0T + \ln(e^{(kN_0\lambda)/L} - 1)$$

where C_0 is the concentration of the adsorbate in the influent carrier gas; C is the concentration of the adsorbate in the effluent carrier gas at the point, λ, the length of the adsorbent column; T, the time for which the gas stream has been flowing; N_0 the number of active adsorption centers per cc. of adsorbent; L, the linear velocity of the gas; and k, is a constant. Therefore, when $\frac{C_0}{C}$ is large, $\ln \frac{1}{C}$ should bear a linear relation to T and the slope of the line would

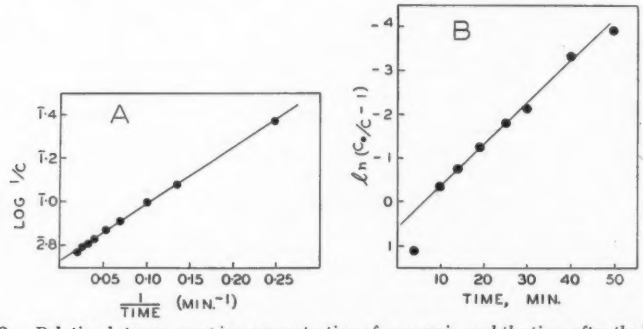


FIG. 13. *Relation between escaping concentration of ammonia and the time after the break time (coconut shell charcoal, 5 cm. bed; sorbate flow rate, 42 cc. per min.; air flow rate, 200 cc. per min.).*
A. Reciprocal of escaping concentration (C) against reciprocal of time.
B. Relation between initial concentration (C_0) and escaping concentration against time.

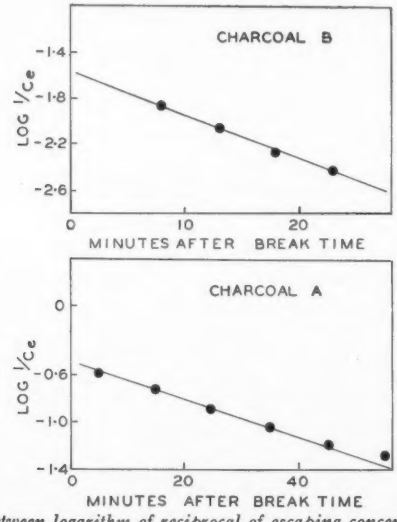


FIG. 14. *Relation between logarithm of reciprocal of escaping concentration (C_e) of cyanogen chloride and the time after the break time (charcoal bed depth, 5 cm.; mass flow rate 500 cm. per min.; adsorbate concentration, $\frac{1}{1510}$ for impregnated coal and wood (B) charcoal, and $\frac{1}{258}$ for coconut shell (A) charcoal).*

give the value of k. Fig. 13A, based on values for effluent concentrations of ammonia after passage through coconut shell charcoal, shows that for this system $\ln \frac{1}{C}$ bore a linear relation to the reciprocal of the time. Plotting $\ln \left\{ \frac{C_0}{C} - 1 \right\}$ provided a closer approximation to theoretical requirements (Fig. 13B). For the system, butane on coconut shell charcoal, $\ln \left\{ \frac{C_0}{C} - 1 \right\}$ was linearly related to the time. Fig. 14 shows that, for cyanogen chloride on either coconut shell or impregnated coal and wood charcoal, $\ln \frac{1}{C}$ bore an inverse linear relation to time.

Determination of the break time is an important practical measurement. With the adsorption balance, it is the point where the time–weight curve first deviates from linearity (Fig. 2). This is not a well defined time and is usually determined as the time at which the adsorbate first appears in the effluent stream, and the limiting effluent concentration is usually arbitrarily selected. It has not been generally recognized that the break time is dependent on the shape of the effluent–concentration–time curve. Fig. 15 shows how three arbitrarily chosen break-time concentrations of 2 mgm. per cubic meter, 20 mgm. per cubic meter, and 60 mgm. per cubic meter would be related to four of these differently shaped effluent–concentration–time curves.

The techniques described here provided accurate determinations of break times which were used to test theoretical predictions (8, 17). One prediction shows that

$$\tau = \frac{1}{kC_0}\left(\frac{kN_0\lambda}{L} - \ln\frac{C_0}{C'}\right)$$

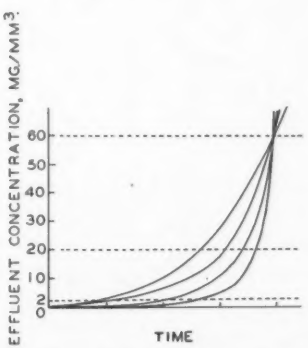


FIG. 15. *Example of possible variation in the determination of break times by arbitrarily chosen concentrations of adsorbate in the effluent stream (broken lines indicate possible arbitrary concentrations).*

where τ is the break time; k, a constant; C_0, the concentration of adsorbate in the carrier gas; N_0, the number of active adsorption centers per cc. of adsorbent; λ, the length of the adsorbent column; L, the linear velocity of the gas; and C', a specified concentration of adsorbate in the effluent stream. According to this relation, the break time should bear a linear relation to the reciprocal of the initial concentration if $\frac{kN_0\lambda}{L} >> \ln\frac{C_0}{C'}$, but should deviate from linearity as C_0 increases. Fig. 16 shows that the linear relation held within the range of initial concentrations used for the adsorption of ammonia

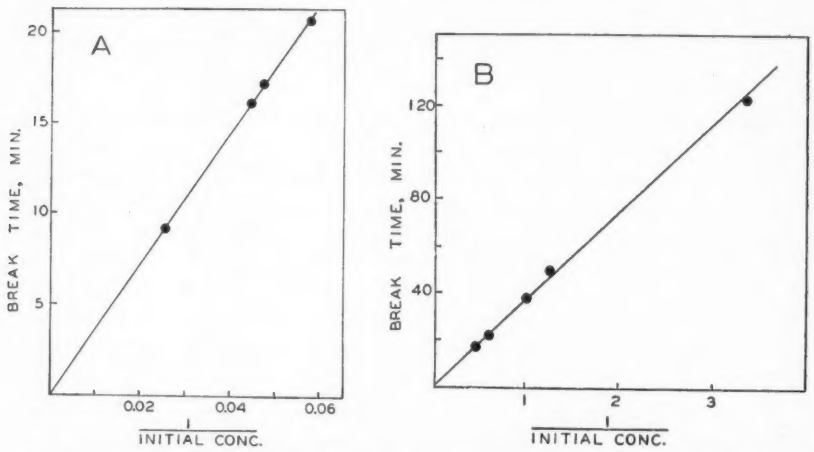


FIG. 16. *Relation between break time and initial concentration of adsorbate for ammonia and butane on coconut shell charcoal.*
A. Ammonia (charcoal bed, 5 cm.; air flow rate, 200 cc. per min.).
B. Butane (charcoal bed, 4 cm.; air flow rate, 3020 cc. per min.).

and butane on coconut shell on charcoal. Fig. 17 shows that the relation was not linear for the range of initial concentrations of cyanogen chloride used on coconut shell and on impregnated coal and wood charcoals.

It has been shown (8) that, if the constant (k) in the foregoing equations is independent of the flow rate,

$$\tau = \frac{N_0\lambda}{C_0}\left(\frac{1}{L} - \frac{1}{L_c}\right)$$

where τ is the break time; N_0, the number of active adsorption centers per cc. of adsorbent; λ, the length of the adsorbent column; C_0, the concentration of adsorbate in the carrier gas; L, the linear velocity of the gas; and L_c is a critical flow rate, beyond which the break time becomes zero. Fig. 18, for ammonia and butane on coconut shell charcoal, supports the application of theory to these combinations. The value of L_c for ammonia adsorption in this system was 4 cm. per sec. while the value for butane adsorption was 10,000 cm. per sec.

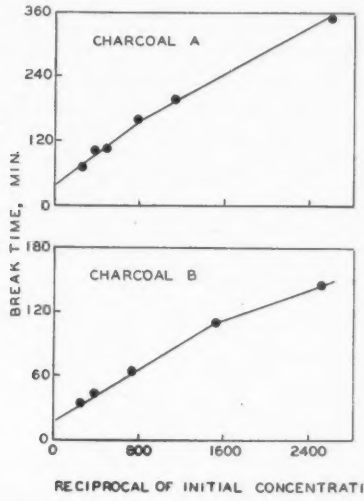


FIG. 17. *Relation between break time and initial concentration of adsorbate for cyanogen chloride on coconut shell (A) and impregnated coal and wood (B) charcoal (charcoal bed, 5 cm.; mass flow rate, 500 cm. per min.).*

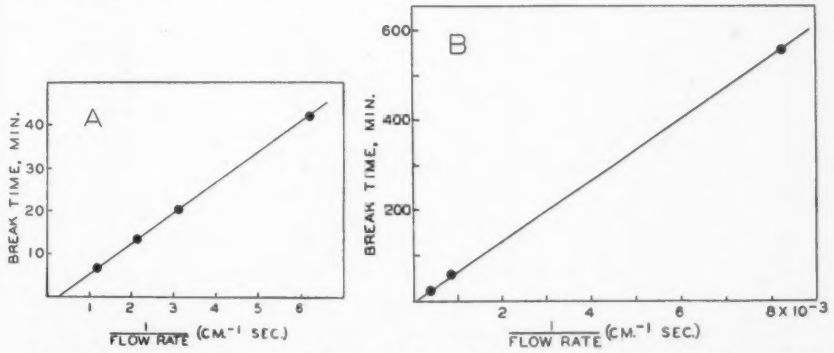


FIG. 18. *Relation between break time and mass (air) flow rate for ammonia and butane on coconut shell charcoal.*
A. Ammonia (charcoal bed, 4 cm.; adsorbate concentration, 16.7%).
B. Butane (charcoal bed, 4 cm.; adsorbate concentration, 1.7%).

Plotting the break time against the column length provides an appraisal of critical length of an adsorbate bed for particular adsorbate and air flow rates as shown in Fig. 19. Since there is a curve into the origin for shallow adsorbent beds, the "critical length" concept is a useful working concept but not a physical entity (11, 15, 16). Theory predicts, however, that the critical length should vary according to the relation (8):

$$\lambda_c = \frac{L}{kN_0} \ln\left(\frac{C_0}{C'} - 1\right)$$

where λ_c is the critical length; L, is the linear velocity of the gas; k, a constant; N_0, the number of active adsorption centers per cc. of adsorbent; C_0, the initial concentration of adsorbate; and C', a specified concentration of adsorbate in the effluent stream. Since in this work C' was a constant value and approached zero, λ_c should bear a linear relation to ln C_0. Fig. 20 shows that this linear relation did not hold for the adsorption of butane on coconut shell charcoal.

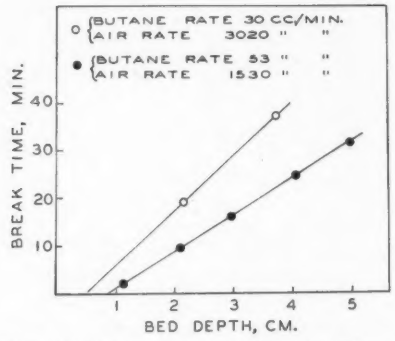


FIG. 19. *Effect of various bed depths on the break time for butane adsorbed on coconut shell charcoal.*

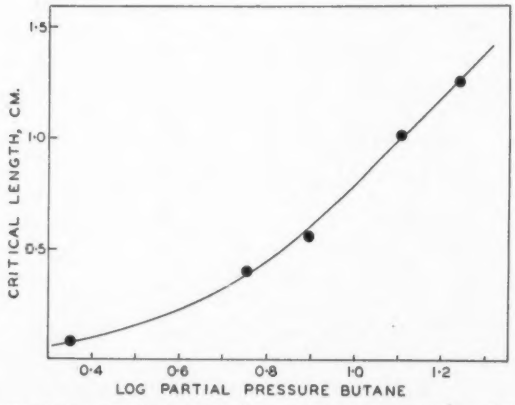


FIG. 20. *Relation between critical length of coconut shell charcoal bed and the partial pressure of butane (mass flow rate, 3050 cc. per min.).*

Desorption of Ammonia and Butane

Four lots of coconut shell charcoal were brought to equilibrium with a stream of pure ammonia. Two lots were desorbed with air: one using 100 cc. per min. through the bed, the other with air at 500 cc. per min. Decreases in the weight held by the charcoal are given in Fig. 21A. The rate of desorption was more rapid with the higher flow rate of air but both reach the same apparent value

of 0.24 gm. of ammonia left per gram of charcoal. Of the two remaining lots, one was desorbed with a stream consisting of 200 cc. per min. of air and 60 cc. per min. of ammonia; the desorption stopped at 0.79 gm. instead of the equilibrium value obtained from the other direction of 0.67 gm. The other was desorbed with a stream consisting of 300 cc. per min. of air and 60 cc. per min. of ammonia, and the desorption stopped at 0.79 gm. compared with an adsoption value of 0.59 gm.

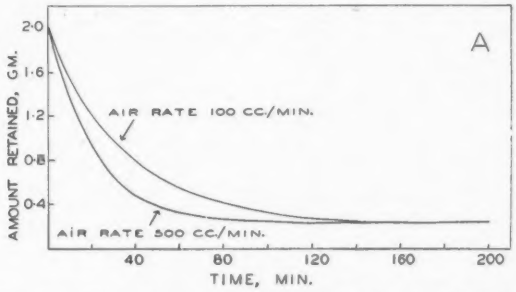
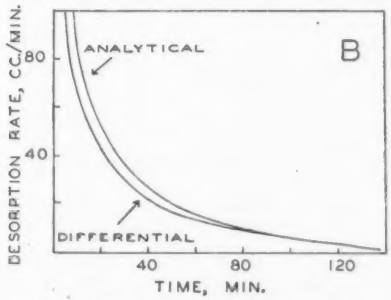


FIG. 21. *Desorption of ammonia and butane from coconut shell charcoal. A. Ammonia (bed depth, 3 cm.).*



B. Butane (bed depth, 4 cm.; air flow rate, 300 cc. per min.).

The desorbing of charcoals, which had been in equilibrium with 60 cc. ammonia and 200 cc. air per min. and with 60 cc. ammonia and 300 cc. air per min., by stopping the ammonia supply, reduced the weight of adsorbed gas from 0.67 and 0.59 gm. to 0.05 gm.

These results indicated that about 90% of the ammonia adsorbed on charcoal is held reversibly and the remainder is held irreversibly or that the apparent irreversibly absorbed ammonia is the result of replacing some of the ammonia by absorbed air.

Coconut shell charcoal, saturated with butane, was desorbed with air at 3000 cc. per minute. The amount held in the charcoal decreased from 6.26 gm. to 0.40 gm. after 30 hr. but equilibrium had not been reached. Limitations in

the apparatus prevented examination over longer periods but the shape of the curves indicated that butane would have been almost completely desorbed if sufficient time had been allowed and, therefore, that butane adsorption is completely reversible.

Fig. 21B shows curves of volume of butane desorbed per minute against time. The lower curve was calculated from the weight–time curves and the upper curve was obtained by analysis of the effluent gas. These curves show that more adsorbate was found in the gas stream than was indicated from the weight reduction. The deviation between the two curves is large at first but gradually decreases to zero. These results present definite evidence to support the assumption that air is displaced from the charcoal by adsorbate molecules during adsorption and replaced during desorption (4).

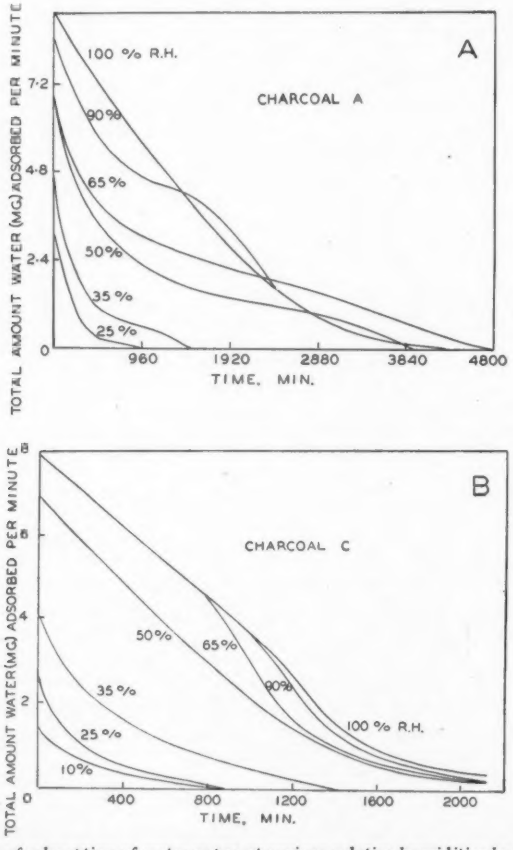


FIG. 22. *Rate of adsorption of water vapor at various relative humidities by coconut shell and impregnated nutshell (C) charcoals (charcoal beds; 5 cm. for coconut shell charcoal, and 3 cm. for impregnated nutshell charcoal; mass flow rate, 500 cm. per min.).*

The Adsorption of Water

The adsorption of water from air streams of 10%, 25%, 35%, 50%, 65%, 90%, and 100% relative humidity on dry coconut shell and on dry impregnated nutshell charcoals was studied in the dynamic adsorption balance cell. This gave such a delicate test of the humidity equilibrium that even an isopiestic method of equilibrium (13) was unsatisfactory and special procedures were necessary to secure accurately regulated humidities in the air stream. The purified air stream was forced through four bubblers in series. Each half-filled bubbler held about one liter of a sulphuric acid – water solution prepared according to existing data (7, 20). The first two bubblers had fine tips and the last two had sintered glass discs to disperse the air. A foot long column of glass wool, which had been soaked in the appropriate solution and drained with the equilibrated air flowing in the reverse direction, acted as a spray trap and a final equilibrator. The specific gravity of the solution in the first bubbler was lowered about 10% by adding excess water. The amount of water used in a given period was calculated and added to the first bubbler regularly, to maintain the concentration constant in the fourth bubbler.

On superficial observation the weight–time curves appeared to be normal, but examination showed that only a fraction of the influent water was removed. Fig. 22 shows the rates of adsorption of water by both charcoals, obtained by differentiation of the weight–time curves. The fraction of the total water removed from the air stream varied from 6.3% to 11.3% and was independent of the relative humidity. This adsorption of a constant fraction suggests linear diffusion as the controlling process.

Fig. 23 shows the adsorption isotherms of water on a coconut shell charcoal containing a trace of silver, on an impregnated nutshell charcoal, and on a set

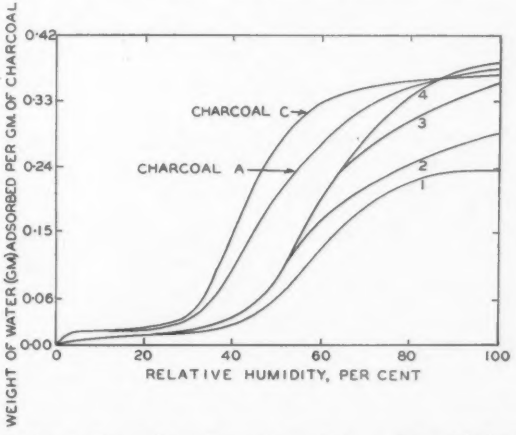


FIG. 23. *Adsorption isotherms for water vapor on impregnated nutshell (C) and on coconut shell charcoals (A) and on coconut shell charcoals containing no silver (bed depths, 3 cm. for charcoal C, 5 cm. for charcoal A, 10 cm. for the others; mass flow rate, 500 cm. per min.; Nos. 1, 2, 3, and 4 refer to 60, 120, 180, and 228 hr. respectively in the steam activator—the longest is considered complete steam activation).*

of unimpregnated coconut shell charcoals activated for 60, 120, 180, and 228 hr. in the steam activator (Nos. 1, 2, 3, and 4 respectively). The S-shaped isotherm is common for vapors adsorbed at or below their boiling points. If a capillary condensation hypothesis (1, 2) is assumed, the diameters of the pores can be calculated from the rapidly rising portion of the curve. The impregnated coal and wood charcoal pores ranged between 11 and 34 Å with the largest number having a diameter of about 15 Å. The unimpregnated, fully activated coconut shell charcoal (No. 4) had pores between 17 and 100 Å in diameter with most of them about 25 Å. Impregnation appeared to effect an appreciable increase in number of small pores.

Temperature Changes During Adsorption

The temperature rise caused by heat of adsorption was assessed by thermocouples. The maximum temperature rise would correspond to maximum adsorption at the position of the thermocouple, if the heat had not been carried away rapidly by the flowing air and if an increase in temperature did not reduce the amount of adsorbate taken up. The production of a maximum temperature depends on the rate at which heat is supplied to any given point by the local adsorption and the rate of the air stream. The time of maximum adsorption rate at any part of the adsorbent bed must, therefore, correspond to some point on the rapidly rising part of a curve showing temperature rise and time. The maximum temperature rise might then be expected when the adsorption wave has passed the thermocouple, if a steady state has been achieved. In addition, Fig. 24 shows that there was a greater heat loss near the bottom of the cell, presumably due to better thermal contact with the surroundings, and that the amount of adsorbing charcoal in front of a thermocouple tended to spread out the maximum in the temperature curve by keeping the heat supply somewhat uniform.

The rise and fall of the temperature might be correlated with the rate of motion of the adsorption wave. An interesting observation was that the temperature maximum of the upper thermocouple occurred at approximately the same time as the break time. All trials did not give good agreement but the observation was of qualitative value in determining when to change the absorbing solutions or sample bulbs.

Since adsorption is greatly affected by changes in temperature, the effect of temperature on the weight–time relations is different at different adsorbate concentrations, air flow rates, and bed depths. This temperature effect prevented accurate determination of the desorption of air during the adsorption process, since the cooling portions of the charcoal bed had an increased adsorptive capacity. The break time may be decreased by disproportionately short adsorbent columns, because of the smaller adsorptive capacity of the heated charcoal. This process may have increased the saturation time of shallow adsorbent beds and might in large measure account for asymmetry in some of the curves of adsorbate concentration in the effluent stream.

It should be pointed out that it is impossible in practice to study thermostated adsorbents in dynamic systems, because of the insulating properties of air and porous adsorbents. For the same reason, thermal junction temperatures may be very different from actual temperatures on any extremely localized surface or inside a charcoal grain. Although the specific temperature effects

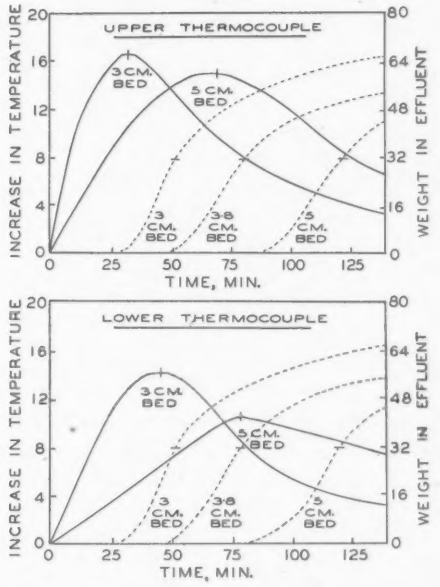


FIG. 24. *Temperature changes in coconut shell charcoal beds contrasted with the quantity of adsorbate in the effluent air stream (air flow rate, 500 cc. per min.; cyanogen chloride concentration* $\frac{1}{253}$).

may differ from the average effects, the maximum temperature rise and the time to attain this temperature in beds of coconut shell charcoal on which butane is being adsorbed have been compared with times for the effluent concentration to become equal to one-half the initial adsorbate concentration (representing the motion of the adsorption wave).

The temperature increments (°C.) for various depths of adsorbent and various air and butane flow rates, using horizontally spaced thermocouples, are shown in Fig. 25. The temperature changes at the center and at a distance of 1.5 cm. from the center of the last layer of a 4-cm. charcoal bed are shown in Fig. 25A. The temperature gradient between the center and a point 1.5 cm. away was negligible during the period of increasing temperature. However, the center of the cell cooled down much more slowly. This behavior was common for the bottom layer at all bed depths.

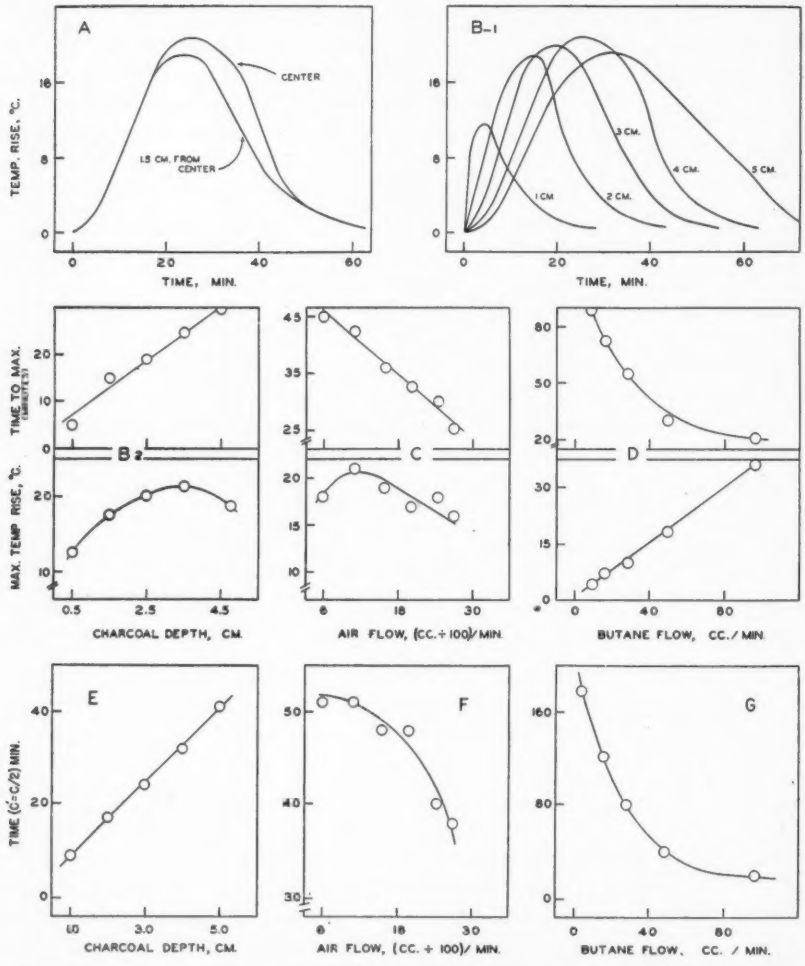


FIG. 25. *Temperature changes in the adsorbent bed during the adsorption of butane by coconut shell charcoal contrasted with changes in the adsorption wave represented by the time required for the adsorbate concentration in the effluent stream (C') to become one-half of the adsorbate concentration (C) in the entering stream.*

A. Temperature difference between center and point 1.5 cm. away (radially) in the last centimeter layer of a 4-cm. charcoal bed (air flow rate, 2650 cc. per min.; butane flow rate, 50 cc. per min.).

B–1. Temperature changes in the last centimeter layer of 1-, 2-, 3-, 4-, and 5-cm. charcoal beds (air flow rate, 2650 cc. per min.; butane flow rate, 50 cc. per min.).

B–2. The important features of curves in B–1.

C. Effect of air flow rate on temperature changes in last centimeter layer of 5-cm. charcoal bed (butane flow rate, 50 cc. per min.).

D. Effect of butane on temperature changes in last centimeter layer of 5-cm. charcoal bed (air flow rate, 2650 cc. per min.).

E. Effect of bed depth on time for C' to equal C/2 for different bed depths and or fixed conditions as in B.

F. Effect of air flow rate on time for C' to equal C/2 for fixed conditions as in C.

G. Effect of butane flow rate on time for C' to equal C/2 for fixed conditions as in D.

Combining data from the separate curves shows that the time of attaining maximum temperature in the center of the bottom layers of various charcoal beds was a linear function of the depth of the charcoal (Fig. 25: B-1 and B-2), as was the time for C' to equal $\frac{1}{2}\ C_0$ (Fig. 25E). However, the maximum obtained was not the same at all depths; the one centimeter layer had only about one-half the temperature rise of the subsequent layers, while the greatest temperature rise occurred in the fourth centimeter layer. This was believed reasonable, since the shape of the curves indicated that the first two layers were cool before the last layer had reached its maximum.

Fig. 25C shows that the time required to attain maximum temperature in the last centimeter of a 5 cm. charcoal bed was a linear function of air flow, and at flow rates above 1100 cc. per min., the maximum temperature attained decreased as the rate of air flow increased. Fig. 25F shows that the time for C_e to equal $\frac{1}{2}\ C_0$ was an inverse curvilinear function of the air flow.

Curves in Fig. 25D and G show that the times required to attain maximum temperature in the last centimeter layer of a 5 cm. charcoal bed and those required for C' to become $\frac{1}{2}\ C_0$ were hyperbolic functions of the adsorbate concentration. The maximum temperature attained increased linearly as the concentration of adsorbate (butane) in the air stream increased.

For ammonia, the maximum temperature rise increased linearly with the increase in the ammonia flow rate at constant air flow rate, and with constant ammonia flow rate and varying air flow rate, the maximum decreased linearly with increase in air flow rate. With constant composition, the maximum increased with increasing mass velocity and appeared to reach an upper limit at a velocity of 600 cc. per min.

Comparative Adsorption of the Various Gases by Coconut Shell Charcoal

From adsorption data for the four gases, the relative areas of coconut shell charcoal required by the different molecules can be calculated. However, each phase of the investigation dealt with particular concentrations and only a fraction of the whole partial pressure range has been covered for any one substance. The relative areas which are accessible to the different molecules are shown in Fig. 26, which expresses the equivalent of plotting the amount adsorbed against the reciprocal of the concentration. A surface area of 1200 square meters per gm. of charcoal was assumed in making the calculations of the surface areas accessible to various molecules. The surface area of the coconut shell charcoal, determined by low temperature adsorption of nitrogen, was 1220 square meters per gm. (14). Butane gives an almost linear relation suggesting compression into a monomolecular liquid layer on the surface covered, while ammonia gives a pressure–volume curve, suggesting a gaseous film. The smallest area accessible to a butane molecule, 50 $Å^2$, is very close to the value of 48 $Å^2$ used elsewhere (12) for close packed butane molecules in a liquid film. The data for cyanogen chloride do not cover a range great enough

to be conclusive but they indicate a type of adsorption intermediate between that of butane and that of ammonia. The very small areas accessible to water molecules is difficult to explain except on the basis of the capillary condensation of bulk liquid into the pores.

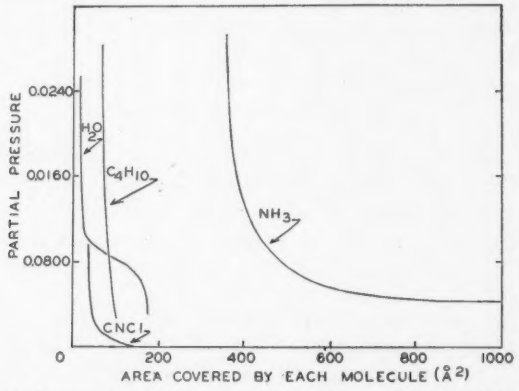


FIG. 26. *Relation between partial pressure of the adsorbate and the area of coconut shell charcoal accessible to different adsorbate molecules.*

Acknowledgments

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